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SIR AMBROSE FLEMING'S METHOD OF ELECTRIFICATION AND ALFRED COEHN'S ELECTROSTATIC EXPERIMENTS

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ABSTRACT. Silica flour poured from a glass beaker or a copper trough carries negative charges away. The silica particles acquire these charges while in contact with glass or copper walls at room temperature. With the sole exception of what is known as "waterfall electrification", cases of electrification through friction or through impact are in fact cases of contact electrification. The sign of the charges separated depends on the work function and the solution pressure of the metal with respect to the dielectric. The action of rubbing an insulator against a metal, for instance, silica in bulk against copper in bulk, can lead to an inversion of the sign of the static charges acquired; the silica can assume a positive charge. This is ascribed to the dependence upon temperature of the migration of positive ions from the metal to the insulator. The action of rubbing thus has two functions: firstly it helps to establish intimate contact between two solids, and secondly, in the atmosphere it abrades particles from noble metals. In addition, in the case of less noble metals the rise of temperature of the surface irregularities increases the ability of the surface of the dielectric to accept positive ions.

SIR AMBROSE FLEMING, F.R.S.[1], described recently a method of creating electrification and emphasized the need for additional research for the purpose of arriving at an understanding of the electrical phenomena involved. Electrostatic charges of opposite sign are separated whenever two different materials are first brought into contact and subsequently taken apart. Two dielectric substances brought into contact acquire electric charges on subsequent separation. Coehn's first rule applies to these cases; it states that after separation the material of higher dielectric constant carries positive charge, while that of lower dielectric constant carries the corresponding negative charge.

The combination dielectric+metal has been investigated by Coehn and Lotz [2], with the result that here the electrochemical character of the metal is of primary importance. In a high vacuum, metals were brought into contact with glass, and the charges that the two materials assumed on subsequent separation

were measured. It was found that base metals as well as their amalgams above a definite concentration acquired negative charges, whereas noble metals acquired positive charges. Pure mercury, for instance, separated from glass is positively charged. An addition of as little as 0·001 per cent of sodium to mercury alters the sign of its charge, whereas the addition of noble metals to mercury preserves its positive charge.

Coehn and Lotz have interpreted their results as the concurrence of two different processes. Metals have a high electron-pressure with respect to dielectrics. They have a tendency to give off electrons to the dielectric with which they are in contact. This process leaves them with an excess of positive charge. Superimposed on this electron transfer is the effect of the solution pressure of the metal, which causes positive ions to be given off to the contacting dielectric. The charge observed results from the superposition of these two mechanisms, which act in opposite directions so far as the sign and magnitude of the separated charges are concerned. Thus, metals of high solution-pressure acquire negative charges against glass, because they give off more ions than electrons. Metals for which both effects almost balance each other prove only feebly charged on separation; copper, for instance, on separation from glass shows only a small positive charge, whereas silver, for which the action of the solution pressure is smaller, separates with a higher positive charge.

Clearly, the ability of the dielectric to accept positive ions must exert its influence too. The fact that dielectrics with a negligibly small ability to accept positive ions act almost exclusively as acceptors of electrons must be considered as support for Coehn and Lotz's hypothesis. Coehn and Curs[3] demonstrated this for diamond, which *always* assumes a negative charge after contact with metals and amalgams of *any* concentration. Even alkali ions cannot penetrate into the lattice of diamond, which, therefore, assumes a negative charge even in contact with sodium amalgam of any concentration.

Coehn and Curs showed that fused silica is a poorer acceptor of ions than glass, and that, among the metals zinc, cadmium, tin, lead, copper, mercury, silver and platinum, zinc was the only one to assume a negative charge with respect to silica. It must therefore be expected that in the experiments described by Sir Ambrose Fleming the silica granules, when they part from their metallic reservoir, carry negative charges with them and leave the metal canister positively charged. Before the falling particles of silica dust impinge upon the perforated diaphragm through which they pass, those among them which have been in contact with the wall of their reservoir have acquired charges. Thus, electrification is observed even without application of either a perforated metal diaphragm or wire gauze.

This point can be checked easily. Stimulated by Sir A. Fleming's paper I connected a metal disk with a home-made electroscope. The metal plate was well insulated. The dust particles (comprising silica flour of two different grain-sizes and flowers of sulphur) were poured out of either a glass beaker or a copper

trough and collected on the metal plate. The particles carried negative charge, although they had not passed a metal diaphragm. It is still possible to assume that they acquired their charge on impinging upon the metal plate. In order to show that this was not the case, the metal plate was covered with a glass plate and the particles were collected on the glass plate. The result was the same. The charges are separated during contact between the dust particles and the container walls. This is further corroborated by the following experiment : instead of pouring the particles from a glass beaker or a copper trough I used a brass tube held insulated in a block of paraffin wax; again the silica flour carried negative charges away. The emptied brass tube showed itself positively charged.

Electrostatic charges are separated wherever *contact* between two different materials is made and afterwards broken. Consequently, electrostatic phenomena are involved in every process of solid friction. Helmholtz has pointed out that the rubbing action itself is important for the generation of static charges only in so far as it creates intimate contact between the two materials. Electrification through friction is a case of contact electricity. The late Prof. Alfred Coehn has designed a pretty demonstration experiment to illustrate this point. He established contact by immersing a solid insulator in a liquid dielectric. Paraffin wax and distilled water are ideal substances for this experiment, because their dielectric constants are widely different, and because paraffin wax is not wetted by water, so that not only complete contact but also complete separation can be established. By removing a paraffin-coated hollow metal sphere from a beaker of distilled water, in which it has been immersed, a considerable deflection of the leaves of an electroscope connected with the metal sphere is obtained. The charge assumed by the paraffin is negative. The water, as the component of larger dielectric constant, retains the corresponding positive charge.

The separation of static charges is thus proved to be the result of processes occurring during *contact*. Electrification follows processes of friction to the extent to which they involve making and breaking of contact. This is obviously the relation of primary importance between the process of rubbing two materials against each other and their electrification. In second approximation, however, the charges separated by frictional contact will not only depend on the number of places of intimate contact created in the act of rubbing. Sir Ambrose Fleming's observations that silica dust sliding over copper carries away negative charges from its contact with the copper, whereas silica in bulk assumes a positive charge after having been rubbed against copper in bulk, suggests that the temperature which the surface irregularities reach, as a result of the heat of friction produced, determines the number of positive ions which the metal transfers to the dielectric. Rise of temperature facilitates ion migration. The local heating of the surface irregularities is undoubtedly higher in the case in which two materials in bulk are rubbed against each other than in that in which fine-grain dust particles slide over a surface. That this interpretation is correct and that the temperature plays an important secondary rôle is proved by the following experiments.

I immersed one end of a piece of silica tubing in mercury at room temperature. When the silica tube was pulled out of the mercury, the end that had been immersed assumed a negative charge. The same end of the silica tube was then held in the flame of a blowpipe, brought to red heat, and immersed again in the mercury while hot. When it was pulled out this time the negative charge it had assumed was considerably smaller. A similar experiment was made by rubbing a piece of silica tubing against a bright piece of solid copper rod under strong manual pressure. At room temperature the silica then assumed a positive charge. Preheating of the silica in the flame just before rubbing it against copper considerably increased the positive charge which it assumed in frictional contact. In agreement with these results and the interpretation given above is the observation that flowers of sulphur acquire a negative charge against glass in bulk, and that sulphur also acquires a negative charge with respect to glass.

Coehn and Curs discussed the influence of the pressure and humidity of the surrounding gas atmosphere upon the charges separated at the contact between solid dielectric and metal, and found that the lower the pressure and humidity the larger is the charge separated, and the better is the reproducibility of the results.

The amount of heat generated through friction is proportional to the load applied. Therefore, under the conditions of Coehn and Curs's experiments, zinc was the only one of the eight metals tested which assumed a negative charge against silica, whereas zinc, cadmium, tin and lead were charged negatively against glass. It is interesting to note that physical development of glass plates over which metals have slid or rolled causes the appearance of traces of the path of frictional contact and that these traces are obtained when either the slider or the roller has been sufficiently heavy by itself, or has by any other means been pressed on to the glass plate sufficiently strongly. A complete theory of solid friction must take into account the molecular mechanisms due to electron pressure and solution pressure that lead to contact potentials.

The observation of positive charges acquired by either silica or glass which in the atmosphere have been rubbed against platinum, leaving the platinum negatively charged, might at first be considered to indicate a contradiction to the hypothesis that the solution pressure of the metal comes into play. However, experiments show that in this case of a metal without solution pressure, particles are abraded from the metal surface and attached to the surface of the dielectric. These particles, which possibly are the carriers of the positive charge assumed during contact, form traces on the surface of the dielectric, which are visible with the naked eye without requiring physical development.

Sir Ambrose Fleming remarks that he could not obtain by an air-blast method results nearly as good as those obtained by his method of allowing streams of particles of insulating material to fall down a tube and strike a sheet of perforated metal or metal gauze. This may be due either to the fact that the air-blast method requires dry air or to the difficulty involved in separating the charged particles

of insulators from the oppositely charged metals. Some years ago Vollrath[4], working in Prof. Millikan's laboratory, suggested the use of the air-blast method in a high-voltage generator. With sufficiently high air-speed to separate the charges, a model apparatus produced a current of 8×10^{-6} amp. at 260,000 v. with a rate of circulation of dust of 1·5 g./sec. Incidentally Vollrath had thereby made use of the contact potential of diatomaceous earth against copper.

The perforated metal or metal gauze in Sir Ambrose Fleming's arrangement can either help to increase the number of charges separated or be of no effect at all. It acts in the former sense if it is hit by uncharged silica particles which have not managed to make contact with the walls of the reservoir before leaving it, and thus obtain their charge at this later stage. If, on the other hand, charged particles hit the diaphragm they will stick to it, unless their weight is too large to be balanced by the electrostatic attraction, and in this case the wires of the gauze or the edges of the perforations will be coated with such particles and the diaphragm will not exert any influence.

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A MECHANICAL DEVICE FOR THE RAPID ESTIMATION OF THE CONSTANTS OF A LENS SYSTEM

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Given simultaneous values of l and l', the distances of an object and its image from a thin lens, the value of the focal length f of the lens is readily determined by a graphical method known as Grubb's construction. The method consists in marking values of l and l' along rectangular axes, joining the points so marked by a line, and locating that point upon the line which is equidistant from both axes. Figure 1 illustrates the method applied to a converging lens, and as (a, a) is on the line it follows that

$$a/l+a/l'=1, \text{ or } 1/a=1/l+1/l'; \text{ i.e. } a=f.$$

In practice it is usual to join points corresponding to more than one set of simultaneous values of l and l', and to determine f from the co-ordinates of the

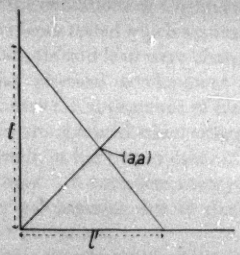

Figure 1.

common point of intersection of the resulting lines.

As an introduction to the study of lens systems it is instructive to extend the method and, by determining some simultaneous values of l and l' measured from the outer surfaces of a system, to record the results on the apparatus illustrated in figure 2. This may be done by the use of clips fastened to the two scales, which are held at right angles in vertical planes and have their zeros coincident.* It may then be observed that lengths of cotton joining corresponding clips and made taut by plumb bobs do not intersect at a point on the line equally inclined to the axes. They may, however, be made to do so by the bodily movement of the scales in their directions by amounts which are determinable by means of the

* The horizontal scale is held just in front of the vertical scale and the clips are so designed that the cottons are coplanar.

auxiliary scales and pointers P and P', and will be denoted by α and β respectively. By analogy with the thin-lens construction it follows that if the distances of an object and its image are measured from points which are themselves distant α and β from the surfaces, i.e. the principal points, then the co-ordinates of the point of intersection of the cottons are (f, f) and the value of f may be determined directly from the scale which is at 45° to the other scales and marked in units of length $\sqrt{2}$ cm.

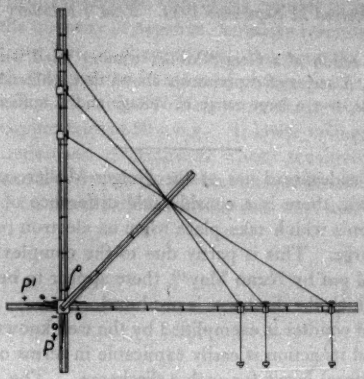

Figure 2.

Thus the apparatus not only indicates the existence of a relation of the form

$$1/(l+\alpha)+1/(l'+\beta)=1/f,$$

but also yields values of α, β and f. As a check on the observations it is, as with a thin lens, advisable to measure more than the minimum number of simultaneous values of l and l', which, being equal to the number of unkowns involved, is in this instance three.

The use of the apparatus for finding the constants of a system separating media of different refractive indices does not call for special comment, since for all lens systems

$$f/(l+\alpha)+f'/(l'+\beta)=1.$$

It may, however, be noted that the co-ordinates (f, f') of the point of intersection of four cottons could not be measured on the 45° scale.

ON THE MODE OF ACTION OF THE GEIGER-MÜLLER COUNTER

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ABSTRACT. The action of a Geiger-Müller counter filled with helium and alcohol has been examined. A series of experiments shows that ionization by collision remains the dominant process over a large range of voltage and is sufficient to account for its action.

In spite of the widespread use of the Geiger-Müller counter for detecting ionizing particles, there is a considerable difference of opinion about the sequence of events which take place when an electron released in it initiates a detectable discharge. This is partly due to the complexity of the problem; as has been pointed out by Nunn May[1], there appear to be at least three quite different ways in which the discharge is produced.

The first type of counter is exemplified by the well known periodic discharge of a neon lamp, and its action is easily explicable in terms of the negative slope of the {current, voltage} curve for such a discharge. The second type, which has been exhaustively studied, has this in common with the first, that the potential-change of the central wire is equal to the over-voltage applied to the counter. A statistical theory which explains the extinction of the discharge in this type of counter in terms of the photoelectrons released at the cathode has been given by Nunn May[2]. Counters of these two types are characterized by the sharp onset of the counting phenomenon at a particular potential difference, analogous to the sudden appearance of the self-maintained discharge between parallel electrodes at the sparking potential. The third type, in which a considerable quantity of alcohol vapour or some similar substance is used to stabilize the counting effect, was carefully investigated by Trost[3]. Some measurements of our own, combined with the results of numerous other authors, enable us to put forward with some confidence a definite suggestion as to the mechanism of this type of counting discharge.

The counters used in this investigation consisted of a thin Pyrex cylinder about 2·5 cm. in diameter, which was rendered conducting by a thin coat of chemically deposited silver. The central wire of 200-μ tungsten was supported at one end from a pinch ; the free end was shielded by a small blob of glass. Before assembly, the wire was thoroughly cleaned in molten sodium nitrite (340° c.) and well washed in distilled water. The whole counter was then baked out under good vacuum conditions for several hours at from 350° c. to 400° c.

The counter was filled with pure helium (at a pressure of 25 to 55 cm. of mercury) and alcohol vapour from a side tube containing alcohol at 0° c. Although this is more troublesome than admitting the requisite pressure of alcohol vapour from a reservoir, the resulting alcohol vapour is much freer from impurities. It may be recalled that most absolute alcohol contains a considerable amount of benzene as well as water; both these substances adversely affect the action of a counter.

By connecting the insulated central wire of the counter to an electrometer we were able to measure the quantity of negative electricity reaching the wire in each discharge and to find out how it changed with the potential difference across the counter. For high voltages the increase of charge on the central wire was directly recorded, for each kick, with a Wolf electrometer in which the silica fibres had been replaced by copper wire of 50 s.w.g. At lower voltages this instrument was replaced by a Lindemann electrometer whose sensitivity was varied by shunting it with mica condensers; at the lowest voltages the size of the individual kicks was too small to be measured directly in this way, and was obtained by

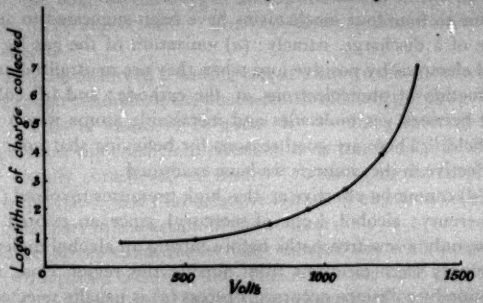

Figure 1.

measuring the ionization current due to a large number of kicks produced by a radium source. There was good agreement between the size of the kick obtained by such integration and the size of a single kick measured directly in that voltage range in which both methods could be used. Since the ionization which was used at the lowest voltages was still being recorded as a series of individual discharges (as observed on an oscillograph) when the full counting voltage was applied to the counter, there can be very little doubt that the figure obtained by dividing the total charge collected at the low voltage by the number of kicks registered at the high voltage does represent the average size of the small kick produced when the potential across the counter is low. The results obtained are shown in the figure. The electricity collected at each discharge at 1350 volts was 0·05 e.s.u.

Consideration of this curve (figure 1) shows that, in contradiction to the obvious interpretation placed upon the characteristic curve (number of kicks against

voltage), counters of the third type have no true starting voltage. The observed sudden onset of counting occurs at a voltage which is characteristic of the amplifier used to register the kicks, and not of the counter itself. This difference between the mode of action of the alcohol-filled counter and the original Geiger-Müller counter, in the working of which a limiting resistance plays an integral part, does not appear to have been generally recognized. It suggests that there is no essential difference between the discharge at low voltages, in which ionization by electron collision is the sole means of multiplication, and the discharge in the counting range. If this is so the secondary processes whose relative importance rises with increasing voltage never attain that control of the production of new ions which they obtain in the self-maintaining discharge. From this point of view the main problem of the mode of action of counters of this type, namely " How is a discharge, once initiated, extinguished? " is seen to be illusory, since a self-maintaining discharge is never established. That this is the case in the particular counters used in this investigation is shown from the following considerations.

From time to time four mechanisms have been suggested to account for the maintenance of a discharge, namely: (*a*) ionization of the gas by positive ions; (*b*) release of electrons by positive ions when they are neutralized at the cathode; (*c*) the production of photoelectrons at the cathode; and (*d*) collisions of the second kind between gas molecules and metastable atoms which have diffused against the field. There are good reasons for believing that none of these processes are effective in the counters we have examined.

Process (*d*) cannot be effective at the high pressures involved (helium, 25 to 55 cm. of mercury; alcohol, 1 cm. of mercury), since an excited helium atom would diffuse only a few free paths before hitting an alcohol molecule, and this would not supply fresh electrons from outside the region close to the wire in which ionization by collisions occurs. Process (*a*) is usually rejected on a variety of theoretical and experimental grounds. If it does occur at all it will be least effective under the conditions considered, i.e., high gas-pressure and positive wire, which will cause the positive ions to wander into weaker electric fields.

Process (*b*), to which the maintenance of a discharge between parallel plates is commonly attributed, can be eliminated owing to the large time (about 10^{-3} sec.) required for the positive ions to reach the cathode. Observation with an oscillograph shows that the counter is again in a sensitive condition at most 10^{-4} sec. after the onset of a discharge, so that process (*b*) would give rise to a series of discharges at 10^{-3}-sec. intervals. These, however, are not observed. That the formation of multiple kicks can actually occur in this way was shown in a series of separate experiments in which multiple counting could be produced at will by introducing minute quantities of xylene into a demountable counter [4].

The maintenance of the negative corona discharge is usually attributed to process (*c*). We believe it not to be important in our experiments for the following reasons. When originally made, the counter was slightly photoelectric, giving

a count of 140 per minute when exposed to strong sunlight. During the course of its use it became much more photoelectric, so that it could only be used when enclosed in a light-tight box. A rough estimate showed that its photoelectric sensitivity had increased at least a thousand-fold. A measurement of its characteristic curve, which had been carefully recorded when it was made, showed no appreciable change. It is permissible to conclude that if the photoelectric coefficient of the cathode can be changed by so large a factor without affecting the working of the counter, the photoelectric release of the electrons at the cathode cannot be playing any important part in its working.

It might be objected that the observed increase in the photoelectric coefficient might be due to a change in the photoelectric threshold rather than to a change in the coefficient. There is, however, independent evidence that this is not so. The counter in question showed the peculiarity that it was more sensitive to the light from a gas-filled tungsten lamp than to sunlight. The frequency region in which there are more quanta in electric light than in sunlight is an extremely narrow one on the edge of the oxygen absorption band, so the threshold is by chance located with great precision. This peculiarity remained after the sensitivity had been enhanced.

Further, from the observed counting rate at a known distance from a 100-watt Osram lamp, a rough estimate of the photoelectric efficiency of the counter surface can be made. This is found to be about 10^{-12}. In spite of the uncertainty of such a calculation the coefficient obtained is so much smaller than the value of about 10^{-5} usually considered necessary [5] to maintain the corona discharge, that it seems improbable that photoelectric release of electrons from the cathode can play any great part in the action of the counter.

Finally, some direct experiments were carried out with a special counter consisting of two separate counting units enclosed in the same envelope [6]. Both counters were photoelectric, and the cylindrical anode of each subtended a large solid angle at the cathode of the other in the envelope. Thus if photoelectrons released by the light from the discharge concentrated near the anode played any part in the action of the counter, one would expect a large number of coincidences between the two sections of the double counters when it was exposed to a γ-ray source. This did not occur; the number of coincidences observed (12 per minute) hardly exceeding the number observed (10 per minute) when two separate counters were exposed in approximately the same relative positions to the γ-ray source. This small difference is more than accounted for by the number of slow electrons which could pass between both counters when they were in the same envelope. As the number of coincidences to be expected on the photoelectric theory was at least 1000 per minute, the result of this experiment is in complete agreement with the rough calculation which indicated that the photoelectric coefficient of the cathode was much too small to have any influence on the maintenance of a discharge in the counter.

It therefore seems clear that the third type of Geiger-Müller counter is a

discharge tube in which a suitable choice of gas and cathode has suppressed all those processes which normally enable a discharge to be maintained. Thus the mechanism of such counters is as simple as possible, and requires no specific explanation.

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THE MOTION OF A MERCURY INDEX IN A CAPILLARY TUBE: PART II

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ABSTRACT. The simple theory of the motion of a liquid index given in a previous paper is in general agreement with observation, and, if accepted, provides an interesting method for the determination of the coefficient of viscosity of the liquid. Experiments on the motion of mercury indexes in soft glass tubes previously described, and also in pyrex and quartz tubes described in the present communication, yield values of the viscosity consistently 6 or 7 per cent higher than the accepted value. The suggestion has been tested that the discrepancy is in some way connected with the electrification of the mercury resulting from its motion. Although the production of electrification clearly affects the motion of a single index, it is shown that a corresponding error in the determination of the viscosity from observations of a number of indexes is eliminated by the mode of calculation. Experiments made to discover whether electrification has any effect on the flow of mercury in a viscometer give a negative result. The discrepancy, therefore, remains unexplained, and doubts are in fact thrown on the validity of the assumptions underlying the theory.

§1. INTRODUCTION

THE motion of an index of mercury in a uniform capillary tube has been studied by West[1] and more recently and in greater detail by the present author[2]. If it be assumed that the radial distribution of velocities is in accordance with Poiseuille's law, except in the region of the ends, a simple treatment of the problem leads to the following expression for the difference in pressure p which must be maintained between the two ends of a horizontal tube of radius a and length L in order to drive an index of length l with a steady velocity v:

$$p=\frac{8v}{a^2}[(l+x)\eta+(L-l)\eta']+\frac{2T}{a}(\cos\theta_1-\cos\theta_2) \qquad \ldots\ldots(1),$$

in which x represents an end correction to the length of the index, η and η' are the coefficients of viscosity of mercury and air respectively, T is the surface tension of mercury, and θ_1 and θ_2 are the respective angles of contact at the two ends of the index. Simultaneous observations of pressure-difference and velocity with a number of indexes are in general agreement with the theoretical relation and, if the theory be accepted, enable a determination of the viscosity of mercury to be made. Alternatively, the accuracy of the value of the viscosity so obtained may be regarded as the supreme test of the theory.

§2. DETERMINATION OF VISCOSITY

The method of observation has been sufficiently described in the previous paper. The coefficient of viscosity η may then be determined from the values of dp/dv given by the experimental curves for a number of indexes in the same tube, since we may write

$$\frac{d}{dl}\left(\frac{dp}{dv}\right) = \frac{8}{a^2}(\eta - \eta') \qquad \ldots\ldots(2).$$

Soft glass capillary tubes of three different radii were used in the experiments described in the earlier paper. Further experiments have since been made with three more tubes, two of pyrex glass and one of quartz. The results obtained with the six tubes are exhibited together in table 1. It appears that for the pyrex

Table 1

Material of tube	Radius (cm.)	Mean divergence (per cent)	Temperature (° c.)	(cos θ_1 − cos θ_2)	Viscosity of mercury (g./cm.-sec.)	
					Measured	Accepted
Soft glass	0·0277	1·1	15	0·32	0·0171	0·0159
Soft glass	0·0503	1·8	15	0·35	0·0169	0·0159
Soft glass	0·1014	1·3	15	0·37	0·0173	0·0159
Pyrex	0·0319	1·1	19	0·42	0·0167	0·0156
Pyrex	0·0548	1·6	19	0·45	0·0167	0·0156
Quartz	0·0605	2·5	20	0·29	0·0166	0·0156

tubes the term (cos θ_1 − cos θ_2) is rather greater than for soft glass tubes, while for a quartz tube it is rather less. The value obtained for the coefficient of viscosity of mercury is consistently 6 or 7 per cent higher than the accepted value at the same temperature. The difference is too large to be accounted for by the ordinary errors of experiment, and an explanation must be sought elsewhere.

In the third column of the table is given the mean divergence per cent of the square of the radius of each tube from the mean of the squares. There does not appear to be any obvious correlation between the error in the determination of the viscosity and the degree of irregularity of the tube. Moreover, experiments made with highly irregular tubes have yielded results less consistent but not on the whole higher than those shown in the table. A simple calculation of the extra kinetic energy imparted to an index when the latter is traversing a slightly wider section of a tube and subsequently lost on passing through a narrow section suggests that any error introduced into the measurement of the viscosity on account of the irregularities not only would be of smaller order than that observed but also would be proportional to the square of the radius of the tube.

§3. THE EFFECTS OF ELECTRIFICATION

In the previous paper it was suggested that the discrepancy might be due to the electrification resulting from the motion of the mercury over the insulating surface of the tube. Although no effect of electrification on the flow of mercury has previously been reported, it has appeared worth while to investigate the

possibility of its occurring. Accordingly, an attempt has been made to measure the electrical charges carried by indexes under various conditions with the tubes used in the determinations of the coefficient of viscosity. Although there are several causes which render an accurate measurement of the charge carried by an index a matter of considerable difficulty, sufficient evidence has nevertheless been obtained to enable the possible effects of electrification on the motion of the index to be discussed. The measurement of the electrification is described fully in another communication[3], and it will be sufficient here merely to summarize the relevant results.

It is found that an index moving with uniform velocity in a clean dry tube acquires a positive charge which is independent of the distance already travelled by the index, provided this distance is greater than 10 or 20 cm. An exactly similar charge is reproduced on subsequent excursions made with the same velocity after the lapse of a few minutes. Moreover, the charge carried is shown to be an increasing function both of the length and of the velocity of the index. On indexes up to 10 cm. in length, moving with velocities up to 20 cm./sec., the charges range from less than 1 e.s.u. to 20 e.s.u. in the glass tubes, while in the quartz and pyrex tubes charges as great as 50 e.s.u. are observed. From the experimental evidence it is concluded that an index moving at a constant velocity becomes charged to a steady potential V, characteristic of the tube, at which the rate of leakage of charge is equal to its rate of generation. The potential V is a function of the velocity but appears to be independent of the length of the index. In the soft glass tubes, V is of the order of a few hundred volts when the velocity is 10 cm./sec. In the pyrex and quartz tubes it is of the order of a few thousand volts.

There are three possible effects of electrification on the motion of a mercury index, which must be examined : (i) An effective increase in the pressure-difference necessary to drive the index with any given velocity, due to the mechanical work which must be done against attractive forces in the separation of the charges ; (ii) an effective reduction in the surface tension at the ends of the index, or an alteration of the angles of contact ; (iii) a modification of the rate of flow of mercury through a tube brought about merely by the fact that the liquid is charged to a high potential.

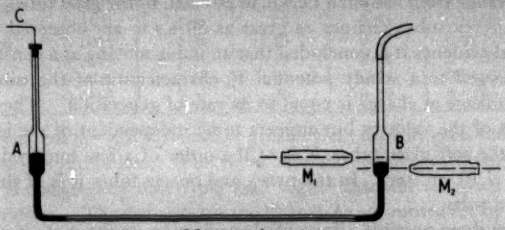
It is necessary, however, to distinguish here between effects which merely modify the flow of a single index and effects which may introduce an error into the determination of the coefficient of viscosity of the liquid from observations of a number of indexes.

The magnitude of the charges involved suggests that the work performed in the separation is appreciable, though clearly it is of less importance in the narrower tubes. Unfortunately, it is impossible to calculate the actual quantity of work done, since the rate of generation of charge is unknown. Nevertheless, the charges $\pm q$ generated by an index in moving a distance of 1 cm. may be assumed to be independent both of its length and its velocity, and may be taken as constant

for any one tube. This assumption is in accordance with the modern view that electrification results from the mere separation of unlike surfaces [4], in this case at the rear end of the index. The work, approximately $2qV$, which is done per centimetre against attractive forces is therefore a function of the velocity but not of the length of the index, since it appears that the potential V depends only on the velocity. Thus an additional term is introduced into equation (1) which is a function of v but not of l. On differentiation first with respect to v and then with respect to l, equation (2), from which the viscosity is calculated, remains unchanged.

Again, as regards the possible effect of electrification on the end surfaces of an index, it is clear that no error arises in the determination of the viscosity, since no term involving the length of the index appears in equation (1).

The existence or otherwise of the third effect suggested above may be established by a study of the flow through a viscometer of mercury which is electrified by some external agency. In such an experiment it is essential to reduce to a minimum the effects which may arise at a meniscus on account of electrification—



Mercury viscometer.

a condition which requires the use of a viscometer in which the menisci move in comparatively wide tubes. The form of the viscometer used in this experiment is shown in the figure. It consisted of two similar vertical glass bulbs A and B, 2·5 cm. in diameter and approximately 7 cm. in height and connected by a horizontal capillary tube of length 50 cm. and diameter about 0·7 mm. The instrument contained about 50 cm.^{3} of mercury which could be displaced from the bulb B to the bulb A by increasing the air pressure in a reservoir connected to B, after which the liquid was allowed to flow back to the bulb B. The mercury could be raised to a potential of approximately 20,000 volts by means of an influence machine driven at a constant rate by an electric motor, connection being made by the iron wire C passing through a loosely-fitting ebonite plug into the bulb A. The whole viscometer was mounted on ebonite blocks, and was not disturbed during a series of observations. Fiduciary marks were provided by the fixed microscopes M_1 and M_2 situated approximately 0·5 cm. and 2·5 cm. respectively below the equilibrium level of the mercury in the bulb B.

A typical series of observations of the time taken by the rising meniscus to move from the level of M_2 to the level of M_1 is given in table 2. The observations

Table 2

Condition of mercury	Observed times of flow (sec.)	Mean time (sec.)	Spread of observations (sec.)
Uncharged	139·4, 139·4, 139·5, 139·2	139·4	0·3
Charged 20,000 v. positive	139·8, 139·8, 139·9, 139·7	139·8	0·2
Uncharged	139·3, 139·4, 139·3, 139·4	139·35	0·1
Charged 20,000 v. negative	139·6, 139·4, 139·5, 139·5	139·5	0·2
Uncharged	139·2, 139·3, 139·3, 139·2	139·25	0·1

were made with a Venner time switch, and their consistency leaves little to be desired. A small unavoidable rise in temperature occurred during the series and showed itself in a slight general decrease in the time of flow. The results show conclusively that electrification to a potential of 20,000 v., whether positive or negative, has no effect on the time of flow of mercury in a viscometer of an order greater than about one part in five hundred. Even this small change may well be due to the effect of electrification on the menisci. Any alteration of the time of flow due to changes in the dimensions of the viscometer which arise from electrostriction are of a much smaller order. It follows that the rate of flow of a mercury index is not appreciably affected by the fact that it is at a higher potential than its surroundings.

§4. CONCLUSION

In conclusion, it may be said that although the motion of a single mercury index must be affected to some extent by its electrification, on account both of the work done in the separation of the charges and also of the change in the surface tension of the liquid, no error is thereby introduced into the determination of the viscosity of mercury from observations of several indexes. The observed difference of approximately 6 per cent between the experimental value of the viscosity and the accepted value remains unexplained. The theory of the motion of an index as given in the previous paper must therefore be regarded as an approximation only. It is possible that a more complete hydrodynamical treatment, which the present author does not propose to attempt, may reveal that the radial distribution of velocities is not in exact accordance with Poiseuille's law, even in the central part of a moving index.

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THE ELECTRIFICATION OF MERCURY INDEXES IN THEIR PASSAGE THROUGH TUBES

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ABSTRACT. The electrical charge developed by an index is found to be a function of its length and velocity and to vary widely with the insulating properties of the material of the tube. It appears that an index moving at a constant velocity becomes charged to a steady high potential, characteristic of the tube, at which the rate of leakage is equal to the rate of generation of charge. The disturbing effect of the method of measurement on the charge to be measured is discussed. A description is also given of a subdivided air condenser having high insulation and a total capacity of approximately 24,000 cm.

§1. INTRODUCTION

It is well known that the motion of mercury over the dry surface of glass or quartz gives rise to electrification and to the production of considerable potential differences. Thus a momentary discharge is frequently observed to take place through the residual gas in a McLeod gauge during the fall of the mercury meniscus. Similarly, electrification results from the motion of a thread of mercury through an insulating tube, as has previously been pointed out by the author [1]. The effect of electrification on the motion of an index is discussed elsewhere [2]. The purpose of the present note is to draw attention to an investigation of the electrification of such an index under controlled conditions. Measurements have been made with a view to determining the electric charges accumulated and the dependence of these charges on the dimensions and material of the tube, as well as on the length and velocity of the index.

§2. EXPERIMENTAL PARTICULARS

In these experiments, six different tubes have been used, all of a high degree of uniformity. Of these, three were of soft glass having internal radii of 0·0277 cm., 0·0503 cm., and 0·1014 cm. respectively, two were of pyrex glass having radii of 0·0319 cm. and 0·0548 cm. respectively, and one was of transparent quartz having a radius of 0·0605 cm. All six tubes were mounted in a horizontal position so that a length of rather more than 120 cm. was available for the excursions of the indexes. The manner of introducing the indexes and of driving them to and fro along the tubes with constant velocity by the pressure of air in a reservoir was similar to that described in an earlier paper [1].

In order to measure the charge carried by an index while in motion an induction method was employed. Surrounding the central part of each tube,

but not touching it, was supported an insulated hollow coaxial metal cylinder of length 14 cm. and internal diameter 1·2 cm., which acted as an inductor. To the inductor, which was screened electrostatically, were connected a Lindemann electrometer, a condenser of known capacity, and an amalgamated earthing key. Initially the inductor was joined to earth while the mercury index was at rest, generally at one end of the tube. The index was then driven along the tube with constant velocity and, after traversing a desired distance, usually about 50 cm., it passed through the inductor. After a little practice, it was found possible to insulate the inductor immediately upon the index being completely inside it, and so to obtain on the insulated system a charge equal and opposite to that carried at that instant by the moving index. The magnitude of the charge was then determined by an electrostatic balance method.

The charges to be measured in these experiments range from less than 1 e.s.u. to 50 e.s.u. In order to avoid leakage during the balancing of the charge it was therefore necessary to keep the potential of the insulated system as low as possible

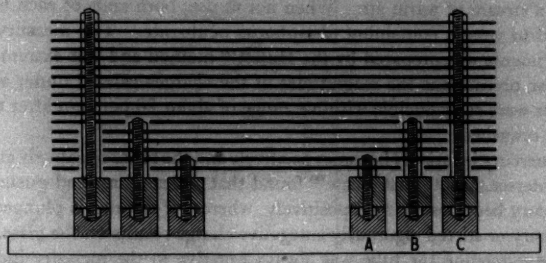

Figure 1. Method of construction of air condenser.

by employing condensers of comparatively large capacity. Condensers containing a dielectric were found to be unsatisfactory, and, finally, a special air condenser, embodying the principle of split insulation, and subdivided to give several different capacities up to a maximum of approximately 24,000 cm., was constructed.

The condenser consisted of two interleaving piles of rectangular aluminium plates laid horizontally and supported by stout vertical threaded steel rods secured to blocks of ebonite on a strong base. Each plate measured 35 cm. by 30 cm. and was approximately 2 mm. thick. The plates of one pile were placed with their long edges perpendicular to the long edges of those of the other pile, so as to leave a strip measuring 30 cm. by 2·5 cm. at each end of each plate by which it was supported. When supported at four points such plates sagged by an inappreciable amount, and it was possible to work with a separation of little more than 1 mm. Adjacent plates in a pile were separated by groups of machined brass washers carefully selected after measurement with a micrometer screw gauge. One pile, consisting of seventeen plates, was subdivided into three

independent sections A, B, and C containing respectively one, four, and twelve plates (figure 1). The other pile, D, not shown in the figure, consisted of eighteen plates in electrical contact. In use, the inductor was connected to one or more of the sections A, B, and C, the remainder being earthed, while the pile D was varied in potential to balance the charge on the insulated system. The whole condenser was enclosed in an earthed metal box which also served to keep light from affecting the surfaces of the ebonite insulators. The condenser was calibrated by comparison with standard condensers of capacities 0·01 and 0·001 μF. respectively, a ballistic galvanometer being used.

The charge carried by an index was found to depend greatly on the state of the surface of the tube, a conclusion which is in agreement with the experience of other investigators[3] of tribo-electric phenomena. In order to obtain the best possible consistency in the measurement of the charges, the tubes were thoroughly cleaned with warm chromic acid solution and concentrated nitric acid and subsequently washed for several days with running distilled water before being dried by a stream of warm air. When not in use, both ends of each tube were connected to vessels containing phosphorus pentoxide. The mercury used in the experiments was prepared by the Hulett[4] method and was extremely pure. With these precautions the magnitudes of the charges carried under any given conditions were reproducible within a range of about 20 per cent after the tubes had been rewashed.

The mercury invariably becomes positively and the tubes negatively electrified. It is of interest to note that Shaw[5] found that a clean glass rod pushed gently into mercury becomes charged positively, whereas if the rod is plunged rapidly into mercury or stirred vigorously a negative charge results on the glass. In the present investigation the tube was always negative to the mercury index, even at the lowest velocities at which observations were possible.

The electric charge carried appears to be independent of the distance already traversed by the index, provided that this is greater than about 10 or 20 cm. Moreover, the charge carried is practically the same during the first excursion in a freshly washed tube as on subsequent excursions at intervals of a few minutes. The remarks to the contrary effect made in an earlier paper[1] were based on observations with tubes which were not sufficiently clean, and they should be discounted. There appears to be no fatigue lasting longer than the time taken to balance the charge. It was observed, however, that the charge carried on the last of a series of excursions made in rapid succession is frequently less than the normal charge. This suggests that any strain[6] produced in the material of the tube disappears after a very short time.

The curves in figure 2 show the manner in which the charge depends on the length and velocity of an index in the six tubes which have been examined. In all cases the charge is greater, the greater the length and velocity of the index. It will be observed that much larger charges are recorded with tubes of pyrex and quartz than with tubes of soft glass.

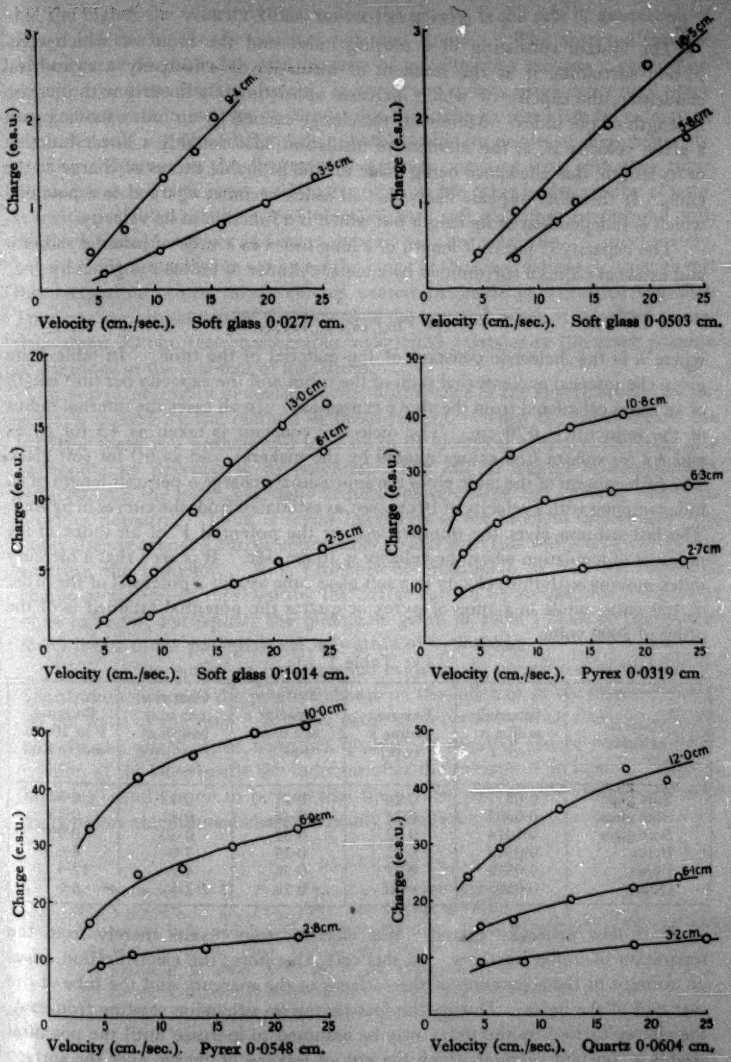

Figure 2. The variation of the charge carried by an index with the length and velocity of the index.

§ 3. DISCUSSION OF RESULTS

The system consisting of a moving index and the inductor which completely surrounds it at the moment of insulation is effectively a cylindrical condenser, the capcity of which increases approximately linearly with increase in length of the index. Moreover, the charge carried by an index moving with a given velocity is, at the moment of insulation, also roughly a linear function of its length, due allowance being made for the probable excess of charge at the ends. It therefore appears likely that an index becomes charged to a potential which is independent of its length but which is a function of its velocity.

The capacity C per unit length of a long index in a tube of internal radius a and external radius b surrounded by a metal cylinder of radius c is given by

$$C = \frac{1}{2\{k^{-1}\log_e(b/a)+\log_e(c/b)\}},$$

where k is the dielectric constant of the material of the tube. In table 1 are given the internal and external radii of the tubes and the capacity per unit length of an index calculated from the above expression. In all cases the internal radius of the inductor is 0·70 cm. The dielectric constant is taken as 4·5 for pyrex and 4·2 for quartz (the values quoted by the makers), and as 6·0 for soft glass. The fifth column of the table gives the approximate charge σ per unit length of an index moving with a velocity of 10 cm./sec. as estimated from the curves in figure 2. The last column gives the quotient σ/C or the potential V of an index at the moment of insulation when the velocity is 10 cm./sec. It is seen that a mercury index moving with this velocity in a soft glass tube attains a potential of the order of 100 volts, while in a tube of pyrex or quartz the potential attained is of the order of 3000 volts.

Table 1

Material of tube	Internal radius a (cm.)	External radius b (cm.)	Capacity c per unit (cm.)	Charge σ per unit length at 10 cm./sec. (e.s.u.)	Potential V at 10 cm./sec. (e.s.u.)
Soft glass	0·0277	0·26	0·37	0·12	0·32
Soft glass	0·0503	0·34	0·48	0·11	0·23
Soft glass	0·1014	0·32	0·52	0·50	0·96
Pyrex	0·0319	0·27	0·35	3·0	8·6
Pyrex	0·0548	0·27	0·38	4·7	12·4
Quartz	0·0605	0·16	0·29	2·5	8·6

It is now generally agreed[7] that electrification results merely from the separation of unlike surfaces. In this case, therefore, the electrification arises on account of the separation of the surfaces of the mercury and the tube at the rear end of the index. During the first part of an excursion starting from rest, the charge carried by the index may be assumed to increase until the potential attains a constant value at which the rate of leakage of charge over the surface of the tube is equal to the rate at which fresh charge is generated. It follows

that the higher the velocity of the index, the greater is the rate of generation of charge and the higher the constant potential attained. The observed increase of the charge on the index with increase of velocity thus receives a general explanation, and the fact that indexes in pyrex and quartz tubes carry very much larger charges than indexes at comparable velocities in soft glass tubes may be attributed to the marked difference in the insulating properties of these materials.

The difference in the shapes of the curves obtained with soft glass tubes on one hand and with pyrex and quartz tubes on the other is also worthy of note. It seems possible that the curves obtained with soft glass may correspond with the electrification in pyrex and quartz tubes at very low velocities. Unfortunately, however, it is not possible to extend the range of the observations in order to test this suggestion, since measurements cannot be made at velocities less than 3 or 4 cm./sec. on account of the sticking of the mercury, while at velocities greater than about 30 cm./sec. considerable uncertainty exists as to the exact position of the index at the moment of insulation.

It is now necessary to consider what disturbance of the charge carried by the index is caused by the method of measurement. When the index enters the inductor there is a pronounced increase in its electrical capacity, resulting in a corresponding decrease in its potential. The rate of leakage is consequently reduced, and the index gradually acquires more charge and tends to rise to its previous potential. Thus, it seems likely that at the moment of insulation the index already carries a charge appreciably greater than that which it carried before entering the inductor. It is probably not justifiable to take the measured charge as accurately representing the charge carried by an index in the absence of an inductor, but equally the potentials given in table 1 must be regarded as lower limits to the potentials actually attained by indexes.

There is not sufficient experimental evidence to permit a discussion of the distribution either of the positive charge on the index or of the negative charge on the walls of the tube. Another cause of uncertainty must therefore remain, namely, the effect of the unknown quantity of negative charge residing on the portion of the tube inside the inductor after the passage of an index. There is, however, good reason to believe that the greater part of this charge has leaked away before the induced charge is finally balanced.

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ON THE EVALUATION OF THE CONSTANTS e, h, m

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ABSTRACT. A recent discussion of the numerical values of the ultimate physical constants e, h, m has been given by Dunnington, which exhibits certain small discrepancies. The present work shows a simpler method of discussion than his, which is attained by considering not the quantities themselves but their logarithms.

§ 1. INTRODUCTION

In a recent number of the *Reviews of Modern Physics*[1], Dunnington discusses at some length the various discrepancies between the different ways of determining the ultimate physical constants e and m, the charge and mass of the electron, and h, the quantum. He makes use of the Birge-Bond diagram in doing this, and arrives at conclusions which I do not wish to criticize. The purpose of the present note is to point out what has long seemed to me to be the best way of studying the subject, certainly much simpler than the one he uses. While this note was in course of preparation there appeared a paper by Du Mond[2] which reviews the subject from very much the same point of view as that which I develop here, but the present method is perhaps sufficiently simpler to merit adoption in any future revision of the constants.

The aim of the work is to derive the best possible values of e, m and h by combining together all the different experimental data. These data yield numerical values for various products of powers of them. In the method of Birge and Bond it is assumed that the Rydberg constant may be used to eliminate m, so that the various experiments may be taken as giving the numerical constants C_n in a set of equations of the form $e=C_n h^n$, where n is some number given ; in fact all lie between 0 and 1. An approximate value of h is assumed and e is plotted against n. Then if the values are all consistent, the points lie on a straight line, the slope of which gives the error in the assumed value of h and then determines e also. This is an elaborate process, and if the results do not fall on a line, it is not easy to see where the error may lie. Furthermore, it is not obvious, without a second calculation of the same data, what effect would be produced by a change of the assumed value of m.

The point of the proposed method is so simple that it is almost disquieting that it has not been used before. It is a troublesome business to think about products, but very easy to think about sums, therefore the natural method of treatment is to use logarithms. Thus an experiment fixes say

$$e^a h^b m^c = D \pm \delta D \qquad \ldots\ldots(1),$$

where the indices are certain given numbers, and D is the experimental value, affected by a probable error δD. This is replaced by

$$a \log e + b \log h + c \log m = \log D + \log (1 \pm \delta D/D) \quad \ldots\ldots (2).$$

If axes are taken for $\log e$, $\log h$ and $\log m$ the equation will define a plane, and the correct values of $\log e$ etc. are given by the intersection of all such planes. Moreover if all the planes but one intersect, and the last does not, there is an immediate strong suggestion of where the error may lie. It may be remarked here that the method of logarithms could with advantage also be used for analyzing the equations of Birge and Bond, if it were thought satisfactory to eliminate m.

The method may be simplified in two important respects. The first is by a shift of origin. To do this it is only necessary to choose values e_0, h_0, m_0 somewhere near the known values and to take $\log (e/e_0)$ etc. as the axial planes. It should be noticed that this does not mean that we are using an approximative method, but merely that we are shifting the origin to a place near the intersection.

The second change is convenient because it is troublesome to make three-dimensional figures. In almost all the experiments m occurs not by itself, but in the combination e/m, and this suggests that $\log (e/m)$ will be a better axial plane to take than $\log m$. With a rather closer inspection of the experimental data it will be found that h almost always occurs in the combination h/e, so that $\log (h/e)$ is better than $\log h$ as another axial plane. We therefore adopt $\log \frac{h}{e}\frac{e_0}{h_0}$, $\log \frac{e}{m}\frac{m_0}{e_0}$ and $\log \frac{e}{e_0}$ as our three *rectangular* axes, and draw our planes with reference to them. It will appear that the majority do not involve $\log (e/e_0)$ at all, and so they are planes lying parallel to the third axis. The intersection of these can be studied in two dimensions before the third dimension is considered at all.

A third point to be settled is as to the base of the logarithms which it is best to use. For the numerical work at the start, of course, common logarithms are used, but the values of e etc. are known so closely that e/e_0 is never far from unity, and differs from it only by something of the order of one part in ten thousand. Consequently there is considerable convenience in the use of natural logarithms, since the final stages of making the corrections become so simple. There is also the advantage that the error in equation (2) becomes simply $\delta D/D$ instead of $0{\cdot}43\,(\delta D/D)$, as it would be with common logarithms.

We therefore write

$$x = 10^4 \log_e \frac{h}{e}\frac{e_0}{h_0}, \qquad y = 10^4 \log_e \frac{e}{m}\frac{m_0}{e_0}, \qquad z = 10^4 \log_e \frac{e}{e_0} \quad \ldots\ldots (3),$$

and equation (2) becomes

$$bx - cy + (a+b+c)z = 2{\cdot}303 \times 10^4 (\log_{10} D - a \log_{10} e_0 - b \log_{10} h_0 - c \log_{10} m_0) \pm 10^4\, \delta D/D \quad \ldots\ldots (4).$$

The first term on the right is put in common logarithms because it is the one calling for accurate numerical work. In every case the bracket reduces to an expression of the order 10^{-4}.

This process gives substantially the same results as those of Du Mond. He assumes approximate values for e, h, m and obtains linear equations between the small departures of the three quantities from these assumed values. The present method differs from his in that his method is approximate whereas this is exact. The distinction is only one of idea and not of practice; nevertheless it does help in clearness of thought not to have to think about approximation, and a further advantage will appear at a later stage. Du Mond also differs in taking as his rectangular axes the directions e, h, m, so that the majority of the equations, which only involve h/e and e/m, lie in a zone along the cube diagonal, and there is just a little trouble in making a clear diagram. If his diagrams were re-drawn with certain oblique axes, they would in principle be the same as the one shown here.

§ 2. PLANES GIVEN BY EXPERIMENT

The experimental data are taken from Dunnington's table VI without further criticism. Some of the columns are reproduced here in table 1. The fifth column will be explained later. An extra row is also added so as to include Rydberg's number, which is not in Dunnington's table.

Table 1

	Experiment	Constant	Value	Other constants *
1	Ruled grating	e	$(4{\cdot}8025 \pm 0{\cdot}0004) \times 10^{-10}$	$Fqck_\lambda^3$
2	Oil drop	e	$(4{\cdot}8036 \pm 0{\cdot}0048) \times 10^{-10}$	cr^{-1}
3	Limit of continuous x rays	h/e	$(1{\cdot}3763 \pm 0{\cdot}0004) \times 10^{-17}$	$k_\lambda rc^{-2}$
4	Ionization and excitation	h/e	$(1{\cdot}3745 \pm 0{\cdot}0013) \times 10^{-17}$	rc^{-2}
5	Radiation c_2	h/e	$(1{\cdot}3730 \pm 0{\cdot}0029) \times 10^{-17}$	$Rc^{-2}F^{-1}q^{-1}$
6	Stefan	$e/h^{2/4}$	$(2{\cdot}0778 \pm 0{\cdot}0020) \times 10^{10}$	$Fqc^{2/3}R^{-1}$
7	Electron diffraction (volts)	$h/e^{1/2}m^{1/2}$	$(1{\cdot}00084 \pm 0{\cdot}00058) \times 10^{-8}$	$r^{1/2}c^{-1/2}k_\lambda$
8	Electron diffraction (velocity)	h/m	$7{\cdot}274 \pm 0{\cdot}016$	k_λ
9	Compton effect	h/m	$7{\cdot}264 \pm 0{\cdot}012$	$k_\lambda c$
10	Specific charge	e/mc	$(1{\cdot}7591 \pm 0{\cdot}0002) \times 10^{7}$	Various
11	X-ray photoelectrons	e^3/mh	$(3{\cdot}8220 \pm 0{\cdot}0029) \times 10^{24}$	$c^3p^3k_\lambda^{-1}r^{-2}$
12	Rydberg's number	e^4m/h^3	$(1{\cdot}666564 \pm 0{\cdot}000083) \times 10^{14}$	c

* See table 2.

We adopt as the rough values

$$\left.\begin{aligned} e_0 &= 4{\cdot}8 \times 10^{-10} \\ h_0 &= 6{\cdot}61 \times 10^{-27} \\ e_0/m_0c &= 1{\cdot}76 \times 10^{7} \\ c &= 2{\cdot}99776 \times 10^{10} \end{aligned}\right\} \quad \ldots\ldots(5).$$

With these values the table yields the equations :—

$$\left.\begin{array}{llll}
1. & & z & = & 5{\cdot}2\pm0{\cdot}8 \\
2. & & z & = & 7{\cdot}5\pm10 \\
3. & x & & = & -5{\cdot}7\pm2{\cdot}9 \\
4. & x & & = & -18{\cdot}8\pm9{\cdot}4 \\
5. & x & & = & -30\pm21 \\
6. & -\tfrac{3}{4}x & +\tfrac{1}{4}z & = & 35\pm10 \\
7. & x+\tfrac{1}{2}y & & = & 5{\cdot}7\pm5{\cdot}8 \\
8. & x+y & & = & 11{\cdot}5\pm22 \\
9. & x+y & & = & -2{\cdot}1\pm17 \\
10. & y & & = & -5{\cdot}1\pm1{\cdot}1 \\
11. & -x+y & & = & -24{\cdot}5\pm7{\cdot}6 \\
12. & -3x-y+2z & & = & -33{\cdot}8\pm0{\cdot}2
\end{array}\right\} \quad \ldots\ldots(6).$$

There are two other planes which might be added to the list, but it seems that their accuracy is too small to help. One of these, mentioned by Du Mond, is the fine-structure constant, which depends on h/e^2; I do not know how accurately this can be measured directly. Suppose that it is

$$hc/2\pi e^2 = 137\pm1.$$

From this we should derive the plane

13. $x-z=9\pm73.$

Another possible plane has not, I think, been noticed; it comes from the Stark effect. The fine structure of this contains a factor h/me, and so gives a plane in

14. $x+y-z.$

Presumably it is impossible to evaluate the electric field with sufficient accuracy to get much out of this, even when advantage is taken of the wide separation of levels which goes with high total quantum number.

The left sides of several of the equations are identical, and we may first co-ordinate these.

1, 2. It is obvious that 1 is so much the better, that 2 could accommodate any value determined by it. In fact it is hardly too much to say that at the present time the most useful function of 2 is to give an accurate measure of the viscosity of the air.

3, 4, 5. The radiation constant of Planck is responsible for 5 and is obviously very imprecise. 3 is much better than 4, and we shall use it, but we may note that 4 suggests that the true value is likely to be more strongly negative than that taken from 3.

8, 9. There is not much to choose between these, and both are very imprecise. A value 5 ± 15 seems a fair compromise.

§3. POINTS OF INTERSECTION

It will be seen that most of the equations do not involve z at all, and we therefore examine the agreement of these first by drawing lines in the plane xy. The lines in question are drawn solid in the figure. At some convenient point on its length each line is crossed by another at right angles which indicates the probable error. The line is thus really to be regarded as a band of this width, inside which the value ought probably to lie, but to simplify the figure the bands are not drawn. It is quite evident from the figure that there is a discrepancy and that some of the experiments must be rejected. Moreover, it is hardly possible to doubt that it is 3 that is wrong. The line 10 is thought to be very good, and if we are to accept 3 as well the intersection is at B. It seems almost impossible that 7 or 11 should admit

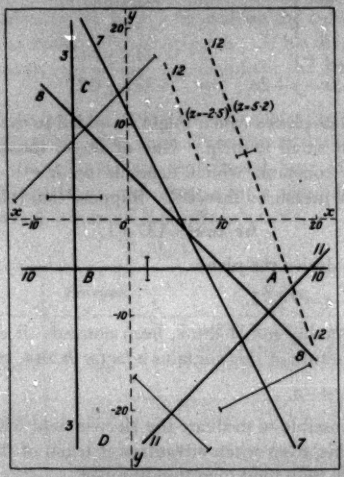

Figure 1. Loci representing experimental data (xy plane).

of this, though 8 might. If on the other hand we decide to reject 10, which signifies that we think the value of e/m is still seriously in error, then we get intersections at either C or D, and the adoption of either means a disbelief in several of the experiments. The diagram thus strongly suggests that it is 3 that is in error. It should be noted that, as far as they go, 4 and 5 support 3 and that their lines suggest, if rather indecisively, a value even further to the left.

We now appeal to the remaining equations, which involve z. The plane 6, which comes from Stefan's constant, is right off the map, for if we put $z=5{\cdot}2$ from 1 we get $x=-45\pm14$. It is true that the error is large, but the most favourable estimate is unlikely to bring it even as far to the right as 3. We are led to believe that Stefan's constant is rather badly in error. The plane 12, which

comes from Rydberg's constant, is subject to practically no error at all, but we are to draw its section by the plane $z=5{\cdot}2\pm0{\cdot}8$ as given by 1. The section of the thin sheet 12 by the thicker sheet 1 gives

$$3x+y=44{\cdot}2\pm1{\cdot}6.$$

The line is shown broken in figure 1, and it is clear that it goes right through the region A, and therefore supports the condemnation of 3.

As a test of how far this support is convincing, let us assume that there is something wrong with experiment 1 and depend on 2. For this, $z=7{\cdot}5\pm10$, and it is therefore distinctly unlikely that z should be less than $-2{\cdot}5$. A broken line corresponding to this is shown in the upper part of figure 1, and it is quite clear that such a line will still pass much nearer to A than to C or any of the other intersections.

The diagram thus almost forces us to the conclusion that there is something wrong with the experiments 3. If this is admitted, then the best values for the constants are given by the intersection of 1, 10, 12, since these are much the most accurate experiments. The solution is

$$x=16{\cdot}4,\quad y=-5{\cdot}1,\quad z=5{\cdot}2 \qquad \ldots\ldots(7).$$

These are the proportional parts in ten thousand to be applied as corrections to h_0/e_0 etc., and the results are

$$\left.\begin{aligned} \boldsymbol{e}&=4{\cdot}8025\times10^{-10}\\ \boldsymbol{e/mc}&=1{\cdot}7591\times10^{7}\\ \boldsymbol{h}&=6{\cdot}6243\times10^{-27}\end{aligned}\right\} \qquad \ldots\ldots(8).$$

In estimating the probable errors in a subject like this it is not worth while to use elaborate processes like adding them by squares. It is good enough to say that $\boldsymbol{e}$ and $\boldsymbol{e/mc}$ have probable errors of one in ten thousand, and as Rydberg's equation is a good deal more precise, the error in $\boldsymbol{h}$ will also be about one in ten thousand.

It is not without interest to note that with these values the fine-structure constant is 137·03, with probable error about 0·03.

§4. INFLUENCE OF OTHER PHYSICAL CONSTANTS

In calculating the numbers given in table 1 use is made of a number of other physical constants, for example Faraday's constant of electrolysis and the absolute ohm. These numbers are thought to be known to a somewhat higher precision than one in ten thousand, but since we have had to admit the existence of an unexplained systematic error, it appears worth looking to see whether any undetected systematic error in any of these quantities would clear up the discrepancy. The method of logarithms is admirably suited to this.

In table 1 the last column gives the dependence of each experiment on these quantities, and their meanings are given in table 2.

Table 2

F	Faraday constant of electrolysis.
p	Ratio of international ohm to absolute ohm.
q	Ratio of international ampere to absolute ampere.
r	Ratio of international volt to absolute volt.
k_λ	Ratio of grating unit to x-ray crystalline unit.
R	Gas constant.
c	Velocity of light.

Dunnington gives the values that he uses, but they are not recorded here because it is only the possibility of unforeseen errors in the accepted values that is of interest. For example, to exaggerate: if future experiments were to show that Faraday's constant had always been taken ten per cent too low, the value of e in 1 and of $e/h^{3/4}$ in 6 would have to be raised ten per cent, and h/e in 5 correspondingly diminished.

All the factors of this type are of course very near unity, and their logarithms are consequently small. We denote them by stars, thus:

$$10^4 \log_e F/F_0 = F^*, \text{ and so on} \qquad \ldots\ldots(9).$$

We now rewrite all the equations, putting in the terms given by the last column of table 1, but transferring them to the left-hand sides of the equations.

$$\left.\begin{array}{rrrrrrrrrrr}
1. & & z & - F^* & - q^* & - c^* & - 3k_\lambda^* & = & 5{\cdot}2 \pm 0{\cdot}8 \\
2. & & z & & + r^* & - c^* & & = & 7{\cdot}5 \pm 10 \\
3. & x & & & - r^* & + 2c^* & - k_\lambda^* & = & -5{\cdot}7 \pm 2{\cdot}9 \\
4. & x & & & - r^* & + 2c^* & & = & -18{\cdot}8 \pm 9{\cdot}4 \\
5. & x & & + F^* & + q^* & + 2c^* & - R^* & = & -30 \pm 21 \\
6. & -\tfrac{3}{4}x & + \tfrac{1}{4}z & - F^* & - q^* & - \tfrac{3}{2}c^* & + R^* & = & 35 \pm 10 \\
7. & x & + \tfrac{1}{2}y & & - \tfrac{1}{2}r^* & + \tfrac{1}{2}c^* & - k_\lambda^* & = & 5{\cdot}7 \pm 5{\cdot}8 \\
8. & x & + y & & & & - k_\lambda^* & = & 11{\cdot}5 \pm 22 \\
9. & x & + y & & & - c^* & - k_\lambda^* & = & -2{\cdot}1 \pm 17 \\
11. & -x & + y & & - 2p^* & + 2r^* & - 2c^* + k_\lambda^* & = & -24{\cdot}5 \pm 7{\cdot}6 \\
12. & -3x & - y + 2z & & & - c^* & & = & -33{\cdot}8 \pm 0{\cdot}2
\end{array}\right\} \quad \ldots\ldots(10).$$

The equation 10 has been omitted, as it is a composite result worked out previously by Birge. The different sources involve a variety of the starred constants. Thus one determination comes from direct magnetic deflection and this will presumably depend on a standard electric current and consequently on q^*, whereas another comes from a comparison of the Rydberg constants of hydrogen and deuterium, which gives the ratio of the masses of electron and atom, and therefore involves F^*.

The starred quantities have a distinctly higher accuracy than x, y, z and it would be out of place to give any weight to equations (10) in evaluating them. The purpose of the equations is to show immediately the effect on all the experiments of a change in one or more of the starred quantities. For example the

equations 5 and 6, which arise from Planck's radiation formula, are the only ones which involve R^*, that is the gas constant, and they both pass far away from the main intersection at A in figure 1. On the other hand their sum cancels out R^* and gives $\frac{1}{2}x+\frac{1}{2}z=5$, which passes right through it, so that a change in the gas constant would reconcile these two equations with the rest. As to the magnitude necessary, if we substitute the value 16 for x in equation 5 we get $R^*=44\pm21$, so that something like 20 or even less for R^* removes the difficulty about 5 and 6. The estimated inaccuracy of the gas constant is about one part in ten thousand, so that this suggestion of a correction twenty times as great can hardly be legitimate, but the case has been cited to illustrate the sort of use to which the equations may be put.

The purpose of setting out the equations (10) is to examine whether any alteration of the starred quantities can improve the intersection in figure 1; in particular whether it can bring the line 3 closer to the rest. We see at once that a change in k_λ^* merely shifts the origin as far as 3, 7, 8, 9 and 11 are concerned, and though 4 is moved differently, this equation is too inaccurate to matter; thus no change of k_λ makes any improvement. As it is 3 that is the trouble, it is natural to try changes in r^* and c^* as the most likely to improve the intersection. Such changes do affect the relative positions of the lines, but trial shows that the discrepancy does not disappear. I give no diagrams, but the reader will find that it is easy in a few minutes to verify it by drawing the lines on squared paper for himself.

§ 5. CONCLUSION

The outcome is exactly that given by Dunnington and Du Mond, that there is a discrepancy between the direction determination of h/e and the other experiments. It seems most likely that there has been some unknown systematic error in the determinations of the limit of the x-ray continuous spectrum. The only alternative is to believe that there are systematic errors in several of the other experiments which happen to give concordant fallacious values. Finally we might think that the work indicates some fault of general theory, but this is a hopeless line to take, for in so doing we deny the validity of most of modern physics, and are then faced with the task of explaining why the concordance of the experiments, even if not perfect, is still quite remarkably good.

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THE OPTICAL CONSTANTS OF THE COPPER-ALUMINIUM α-ALLOYS

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ABSTRACT. Experimental values of the optical constants (refractive index, extinction coefficient, absorption coefficient, and reflecting power) are given for some Cu-Al α-alloys. Curves showing the variation of the constants with wave-length are shown, and the interpretation of the results is discussed briefly.

§1. INTRODUCTION

In continuation of the experimental investigation into the optical constants of simple binary alloys[1], [2], this paper deals with the measurement of these constants over the range 5000 A. to 9500 A. for alloys in the α phase of the Cu-Al system. Commercially these alloys are known as the "aluminium bronzes", and according to the phase diagram of the alloy system as determined by Stockdale and others[3], alloys containing up to 10 per cent by weight of aluminium lie in the α phase. If the weight of aluminium is increased beyond 10 per cent the alloy contains more than one phase, and, as has been pointed out by Lowery and his co-workers, a two-phase alloy must consist of separate microscopic particles lying side by side and reflecting light independently of each other. The optical constants of such an alloy cannot receive any simple interpretation, but those of a single-phase alloy can be interpreted directly like the correspond ng constants of a pure metal. Accordingly in the present case measurements have been made only on α-phase alloys containing up to 8 per cent by weight of aluminium.

§2. EXPERIMENTAL METHOD

The constants were measured by a new photoelectric method developed in the Physics Department of the College of Technology, Manchester, and described in a recent paper by Bor, Hobson and Wood[5]. The method is based on the katoptric method due to Drude[4], and the optical constants—refractive index n, extinction coefficient K, absorption coefficient nK, and percentage R of incident light reflected—are calculated from the observed quantities θ, Δ and 2ψ, where θ is the angle of incidence of light on the specimen, Δ is the phase difference between the components of the elliptically polarized reflected light, and ψ is the azimuth of the restored plane-polarized light. Measurements were made up to 9500 A, and a complete measurement of a specimen required 4 to 5 hours' continuous observation. Each specimen was measured immediately after polishing, and

no change in Δ or 2ψ due to decay of the polished surface could be detected during measurement. Each specimen was polished, measured, etched with acid ferric chloride solution, repolished, and measured again. The results shown are the mean values of the two independent measurements.

§ 3. PREPARATION AND TREATMENT OF SPECIMENS

The specimens were prepared some years ago in the Metallurgical Department of the College of Technology, Manchester, by melting calculated weights of pure electrolytic copper and aluminium of 99·6 per cent purity in a Morgan crucible under graphite. The alloys were cast in cylindrical moulds, and pieces of suitable size were machined out and annealed in a gas muffle furnace by heating to 800° C. for 24 hours and then cooling over a period of 18 hours. The specimens so produced, 1 in. in diameter and $\frac{1}{2}$ in. thick, were of suitable form, and analyses (made by estimating the copper electrolytically and the aluminium as oxide) gave the compositions quoted in table 1.

Table 1

Specimen	Aluminum (per cent by weight)	Copper (per cent by weight)	Aluminium (atoms per cent)
A	2·095	97·85	4·81
B	4·25	95·85	9·49
C	6·13	94·04	13·36
D	8·17	92.05	17·37

After preliminary grinding, the specimens were polished first with successively finer grades of French emery papers of grades 0 to 0000 F., and finally on damp Selvyt cloth impregnated with magnesia. Alternate etching with acid ferric chloride solution and careful polishing on the Selvyt cloth removed all fine scratches and polishing marks. After a first complete polishing, all specimens were annealed at temperatures just below their melting points for from 70 to 75 hours to remove cold working, and were then repolished starting from the 00 F stage. An attempt was made to give all specimens a consistent polish and at the same time to avoid heavily flowed-over surfaces.

§ 4. REVIEW OF RESULTS

Preliminary curves of nK and n against wave-length showed that all specimens had minimum values of these constants between 5000 A. and 7000 A. Beyond 7000 A. the curves ran smoothly up to 9500 A. Results for the 5000 A. to 7000 A. region were treated more thoroughly by plotting observed compensator readings and values of 2ψ against wave-length, and drawing a smooth curve through the points. Then with values from the graphs the optical constants for wave-lengths 5000 A., 5200 A., 5400 A. . . . . 7000 A. were calculated. This treatment of the observations enabled the positions of the minima in n and nK curves to be located accurately.

Figures 1 to 4 show n, K, nK and R respectively for all specimens over the range 5000 A. to 9500 A.

All values shown are actual experimental results except those in figure 2, in which the curves have been conveniently separated from each other by the subtraction of constants from the actual experimental values.

§ 5. ABSORPTION COEFFICIENT nK (figure 3)

The minimum values of nK and their positions are shown in table 2. In specimens A and B the rate of approach of nK to its minimum value is rapid, and the absorption edge is well defined, but in specimens C and D the rate of approach is much smaller, the absorption edge being broadened and its exact position

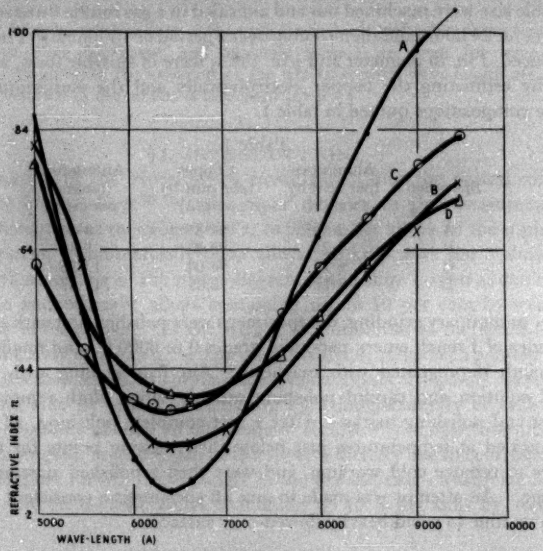

Figure 1.

difficult to determine. In table 2 the minimum is placed at 6000 A. for both specimens, although curves drawn on a bigger scale indicate that it may perhaps lie below 6000 A. The minimum values of nK increase as the weight of aluminium increases.

Table 2

Specimen	Position of minimum (A.)	Minimum value of nK
A	6300	0·735
B	6100	0·905
C	6000	1·155
D	6000	1·255

§6. REFRACTIVE INDEX *n* (figure 1)

All specimens show a minimum in refractive index, though the position of the minimum does not vary regularly. Table 3 gives the positions of the minima along with the actual minimum values of *n*, the latter increasing as the weight of aluminium increases.

Table 3

Specimen	Position of minimum (A.)	Minimum value of *n*
A	6400	·236
B	6200	·308
C	6400	·367
D	6700	·387

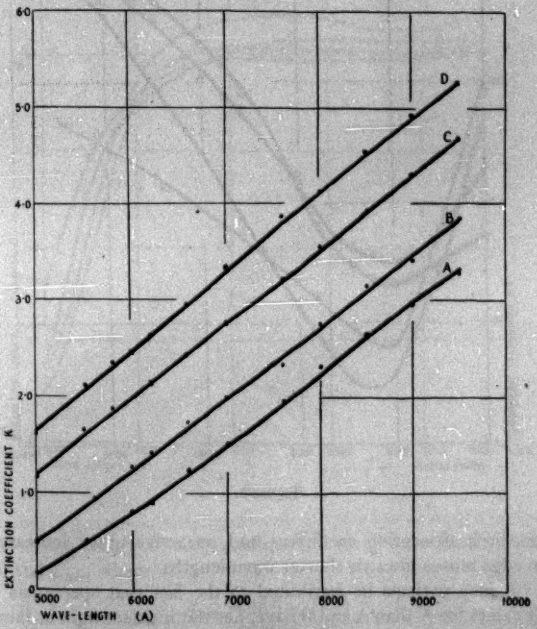

Figure 2.

§7. EXTINCTION COEFFICIENT *K* (figure 2)

In all specimens *K* varies almost linearly with wave-length. Specimens A and B have almost identical values, as have specimens C and D, the latter having higher values than A and B. The constants, subtracted from the actual experimental values in order to separate the curves conveniently, were as follows :

A=2·0, B=1·5, C=1·0, D=0·5.

§ 8. REFLECTING POWER R (figure 4)

All specimens show the same variation in R, i.e. R increases rapidly up to 6500 A., and beyond this wave-length remains nearly constant at about 90 per cent. The values of R throughout are high, and along with the low values of refractive index indicate success in avoiding heavily flowed-over surfaces during polishing.

As aluminium is added to copper three effects may be noted : (*a*) the rate of approach of nK to its minimum value, i.e. $d(nK)/d\lambda$ decreases, the absorption edge becoming less sharp ; (*b*) near the absorption edge, and on its longer-wave-

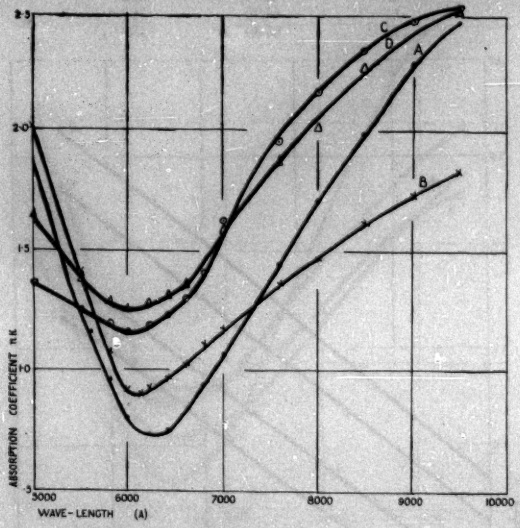

Figure 3.

length side, both absorption coefficient and refractive index increase; (*c*) the absorption edge moves towards shorter wave-lengths.

Effect (*a*) may perhaps be attributed to the fact that specimens C and D have larger values for K than A and B have, i.e. the incident light is damped more rapidly in C and D. If we regard the electrons of a metal or alloy as free to oscillate under the action of the incident light, then the amplitude of the forced vibrations will be a maximum when the frequency of the incident light is equal to the natural or free frequency ν_0 of the electrons. For small values of K the forced amplitude will vary rapidly near ν_0, but as K is increased the response near ν_0 becomes less accentuated, i.e. the peak in the {amplitude, frequency} curve is broadened. This reasoning can account for the effect shown in the

$\{nK, \lambda\}$ curves if it is remembered that nK represents the absorption of energy from the incident light and that the considerations are applied to the longer-wave-length limit of an absorption band in the ultra-violet.

Effect (*b*) is due probably to the increasing resistance of the alloy as aluminium is added, which must give rise to greater absorption. If this is taken into account in applying dynamical theory to the interaction between the electrons and the incident light, the increase in refractive index also may perhaps be explained.

Effect (*c*) can be explained by means of the electron theory of metals in a manner similar to that used by Mott in the case of the copper-zinc alloys[6].

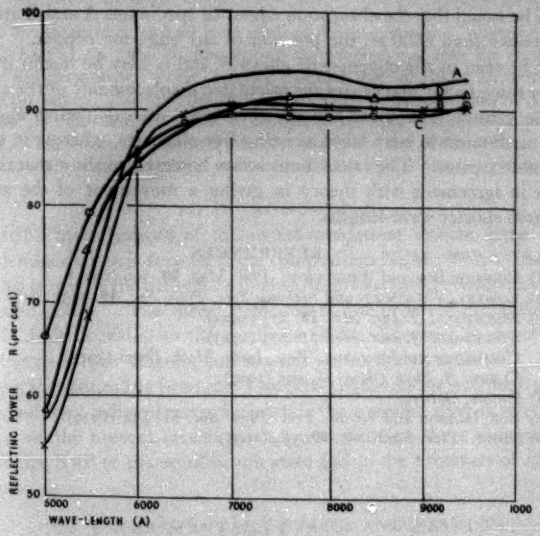

Figure 4.

According to this theory all the electrons in a metal have kinetic energies lying between 0 and E_{max} where

$$E_{max} = 36{\cdot}1 \times \left(\frac{n_0}{\Omega}\right)^{2/3},$$

n_0, being the mean number of free electrons per atom and Ω the volume per atom multiplied by 10^{24}. An electron added to the metal cannot have energy less than E_{max}, and as aluminium is added to copper, n_0 increases faster than Ω, giving increasing values of E_{max} with consequent movement of the absorption edge towards shorter wave-lengths as the weight of aluminium is increased. If we take the absorption edge for pure copper to be at 6000 A.[5], the calculated

displacements of the absorption edge in each of the four specimens are as shown in table 4.

Table 4

Specimen	Aluminium (atoms per cent)	E_{max} (ev.)	Position (A.) of absorption edge	
			calculated	observed
Pure copper	0	6·98	—	6000
A	4·81	7·22	5400	6300
B	9·49	7·44	4900	6100
C	13·36	7·60	4600	6000
D	17·37	7·74	4350	6000

It will be noted that the absorption edges for specimens A and B are at wave-lengths greater than 6000 A., the position of the edge for copper. The same effect can be seen in the copper-zinc alloys[2], and it may be due in the present case to the same factor that causes the calculated displacements of the absorption edge to be greater than those actually observed. In calculating E_{max} the $3s^2$ electrons in aluminium were taken as being free electrons, whereas in actual fact they probably are not. The calculations serve, however, to show that the present results are in agreement with theory in giving a movement of the absorption edge towards shorter wave-lengths.

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THE ORDER-DISORDER TRANSFORMATION IN THE ALLOY Ni_3Mn

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ABSTRACT. Measurements have been made of the magnetization, electrical resistance and specific heat of the alloy Ni_3Mn during the progress and after the completion of a variety of heat treatments. The evidence indicates that at 510° C. an order-disorder transformation occurs, and that the ordered structure is ferromagnetic with a Curie point at 460° C. The sharp decrease of resistance on slow cooling takes place at the Curie point. The effect of the degree of order and of the size of the ordered regions on the resistance and the magnetization is discussed in the light of the experimental results.

§1. INTRODUCTION

Previous investigations of the nickel-manganese system have suggested that a superlattice is formed at the composition Ni_3Mn [3], [7]. The evidence for this is mainly the difference in electrical resistance between the quenched and annealed alloys. The direct detection of the ordered structure by x-ray methods is difficult owing to the smallness of the difference in atomic number between the two types of atom, and has not yet been accomplished. It has also been shown that annealing produces a marked change in the magnetic properties, the quenched alloy being paramagnetic while the annealed alloy is ferromagnetic. The object of the present investigation was to examine these changes in detail, with reference both to the equilibrium state and to the processes of approach to equilibrium.

§2. EXPERIMENTAL DETAILS AND RESULTS

With this end in view, an apparatus was constructed to enable simultaneous measurements to be made of the resistance and the magnetization. The specimen, in the form of a wire about 0·5 mm. in diameter and 10 mm. long, was supported on a Sucksmith balance so that it lay across the lines of magnetic force at a point where the vertical field gradient was a maximum. The use of this method of measuring the magnetization of ferromagnetics has recently been discussed by Sucksmith [6], and needs no further comment here. The shape of the specimen in our case was determined by considerations of convenience in the measurement of its resistance, and its disposition in the field was governed by the necessity of having H and dH/dx as far as possible constant over its whole volume. The consequence was that the demagnetizing factor was large (actually 2π), but this does not constitute a serious objection to the method, for precision measurements

have not been attempted. It is usual to give the results of such measurements by quoting the saturation magnetization σ extrapolated back to zero internal field (i.e. applied field corrected for demagnetizing field). In the neighbourhood of the Curie point the extrapolation must be done by indirect methods which involve measurements made at different temperatures [8]. This process is *a priori* inapplicable to a substance whose structure changes with temperature, and so the simpler course has been adopted of quoting the value of σ in an (internal) field of 10,000 oersteds. The difference is that the abruptness of a Curie point is smoothed out, and the magnetizations at higher temperatures are all rather too large.

The resistance was measured by the usual current-and-potential method, but owing to the small size of the specimen it was not considered worth while to determine absolute values. Accordingly all resistances are expressed on a scale which makes the value at 600° c. equal to unity ; this temperature is chosen as being well above the critical temperature. The current leads to the specimen were made of platinum wire, and the potential leads of platinum-rhodium alloy, so that by a suitable switching arrangement they could also be used to measure the temperatures of the two ends. One further experimental point may be mentioned. An evacuated electric furnace surrounded the specimen between the magnet poles to enable observations to be made at high temperatures, and most of the various heat treatments to be described were given to the alloy *in situ*. Consequently it was not practicable to obtain a quench into water in the normal manner. When, however, the furnace current was switched off, the temperature fell to half value in about 30 seconds, and it will be shown later that the rate of relaxation of the alloy is so slow that this rate of cooling is almost equivalent to a proper quench. This procedure will be referred to in what follows as " rapid cooling."

The materials used were electrolytic nickel, kindly supplied by the Mond Nickel Company and quoted by them as 99·92 per cent pure, and Hilger manganese (Lab. No. 9448), 99·99 per cent pure. These were melted together in an alumina crucible by means of a vacuum induction furnace, and pieces of the ingot were remelted in an alumina tube wound with molybdenum wire so that the material might be obtained in the form of a rod. This was hot-swaged down to about 2 mm. cross-section, and the specimens were either turned or ground from the resulting material. After being prepared they were sealed in evacuated quartz tubes and annealed for several hours at about 1000° c. to remove any traces of coring which remained. During these processes of preparation part of the manganese content was lost, but an analysis of the final material gave the composition as 25·6 atomic per cent of manganese.

As a preliminary step, measurements were made on a rather larger piece of the material to give the {resistance, temperature} relation for the equilibrium state of the alloy. The results are shown in figure 1. The cooling from 625° c. to 310° c. took place over a period of 9 days, but not at any steady rate. These

measurements showed that some slow change was taking place in the material, since if the temperature was changed quickly the resistance took some time to reach its final steady value. They also showed that a good approximation to the equilibrium state had been reached, at least at the higher temperatures ; the point at 459° c. (marked with a cross), for example, which lies quite well on the curve, was obtained after the alloy had been reheated from 410° c. and held at the higher temperature for 240 minutes. The upper portion of the curve is shown on a larger scale in the inset, together with some less complete results obtained later on other specimens which were not cooled quite so slowly (▽ and □). It will be noted that the point at which the resistance begins to fall rapidly is by no means

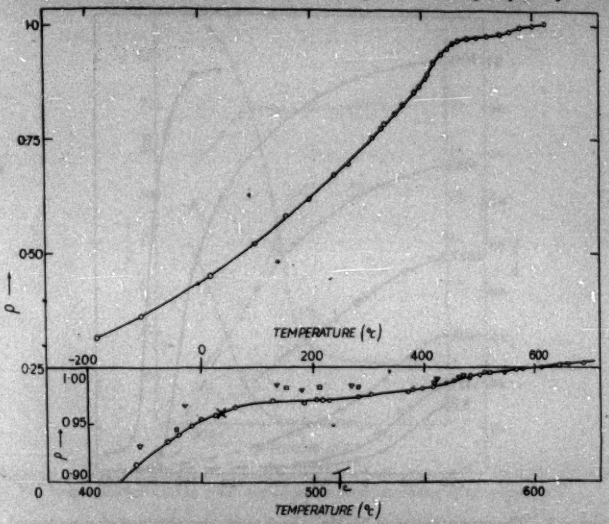

Figure 1. The equilibrium resistance of Ni_3Mn from −200° c. to 600° c. Inset, the upper end of the curve on a larger scale.

sharply defined, but can only be said to be in the neighbourhood of 460° c. This is evidence against the interpretation that 460° c. is the critical temperature for an ordering process, although it must be admitted that at least one other example (Cu_3Pd) is known where the resistance curve shows no sharp bend.

With the apparatus described above, the variation of magnetization with temperature was next investigated. The procedure adopted was to anneal the specimen *in situ* at a constant temperature until the magnetic (and, where available, resistance) measurements indicated that no further change was taking place. The specimen was then cooled rapidly to room temperature, and the variation of σ with temperature was investigated for the existing state of the material over

a temperature range limited at its upper end by the necessity of preventing further changes in the state. The whole process was then repeated at a lower annealing temperature. The results obtained are shown in figure 2. (As before, the crosses on the curve for 488° c. represent measurements made when the state was approached from a lower temperature, the coincidence showing the attainment of equilibrium.) All points on the diagram marked with the same symbol thus have the same structure, while the curve A gives the equilibrium value of σ corresponding to each temperature T. It will be observed that the Curie point occurs at about 460° c., at the same temperature as the maximum curvature of the resistance graph. But what is perhaps more interesting is the

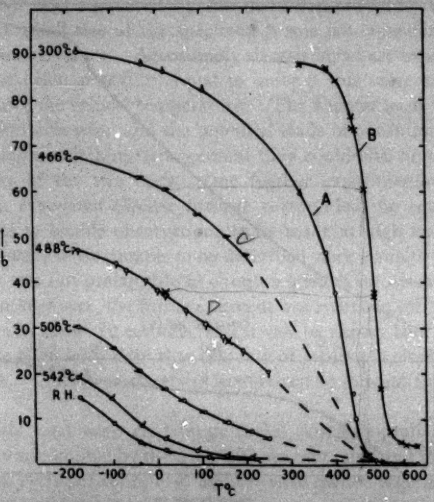

Figure 2. The magnetization of Ni_3Mn. Each curve was obtained after prolonged annealing at the temperature shown at its upper end. For A and B, see the text.

fact that important changes are taking place in the alloy for fifty degrees above this point. This is clearly demonstrated by the fact that, when the alloy is annealed in this region and then cooled rapidly to room temperature, the value of σ obtained depends greatly on the temperature at which the anneal was carried out. This is shown in curve B, figure 2, where σ, measured at 17° c., is plotted against the temperature of the preceding anneal. These measurements, all made under identical conditions, can, it is suggested, correspond only to differences in the structure of the alloy, such as different degrees of order. On this view, the critical temperature for the ordering process is about 510° c. Quenching effected from above this temperature preserves the disorder and the paramagnetic

state. Below it, the degree of order and, correspondingly, the saturation magnetization at room temperature, increase as the annealing temperature is reduced, but for all states of order the Curie point is in the neighbourhood of 460° c. The results obtained by Kaya and Kussmann[3] are consistent with these conclusions. The rapid fall in resistance near 460° c. is therefore to be associated with the transition of the ordered alloy through its Curie point, whilst the order-disorder transition has little or no direct effect on the resistance.

To check these conclusions, a third series of experiments was made to obtain simultaneous measurements of σ and ρ, as these were incomplete for the previous specimen. Figure 3 shows the results, A and B being the equilibrium values

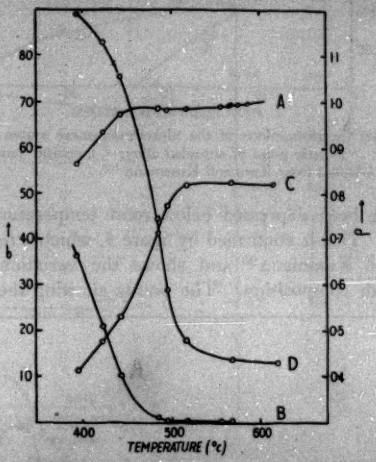

Figure 3. Resistance (A) and magnetization (B) at temperature T. Resistance (C) and magnetization (D) at room temperature after annealing at temperature T.

at a temperature T, while C and D are the values at room temperature, after prolonged annealing at T followed by rapid cooling. It will be seen that the correlation between the changes of magnetization and resistance is exceedingly close in both sets of measurements.* A careful re-examination of the resistance results, figure 1, shows no singularity near 510° c., the suggested order-disorder transition, and no satisfactory explanation has yet been advanced as to why the ordering process has so little direct effect on the resistance.

The lowest curve on figure 2, marked R.H., was obtained after the specimen had been quenched into water from a red heat (say about 700° c.), and it will be seen that it is not markedly different from the one immediately above it, in spite of the fact that the rates of cooling must have differed by a factor of at least

* This parallelism extends also to the dependence of the two quantities on the degree of cold work, both for the quenched and for the annealed alloy, as has been shown by Dahl [1].

100. Thus we can with some confidence regard the process of rapid cooling as being almost equivalent to a quench. It will further be noted that below room temperature even the quenched alloy becomes appreciably ferromagnetic. This, it is suggested, really represents the ferromagnetism of the nickel, the

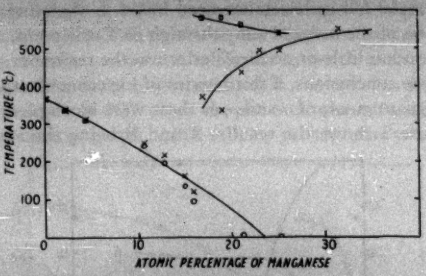

Figure 4. The magnetic transformations of the nickel-manganese system. ⊙, Curie point of quenched alloy ; ×, Curie point of annealed alloy; □, critical temperature for order-disorder change. Adapted from Kaya and Kussmann [3].

Curie point having been depressed below room temperature by the addition of the manganese. This is confirmed by figure 4, which is reproduced from the paper of Kaya and Kussmann[3] and shows the variation of the magnetic transformations with composition. The points showing the suggested order-

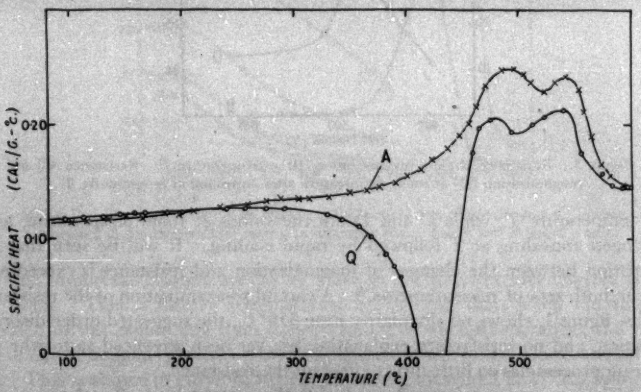

Figure 5. Specific heat of Ni_3Mn. Q, specimen quenched from 575° c.; A, specimen slowly cooled, 600° c. to 350° c. in 14 days.

disorder transitions have been deduced from the other data given in the same paper and have been added to the diagram.

Measurements of the specific heat by Sykes' method confirm the opinion

that we have to deal with two critical temperatures.* The two maxima in the specific heat of the annealed alloy (figure 5, curve A) are well defined, but both seem to occur at temperatures higher than those given above for the critical points, 490° c. and 540° c. as against 460° c. and 510° c. The quenched alloy shows a negative specific heat round about 420° c. This merely means that at the rate of heating employed ($1\frac{1}{2}$ degrees per minute) the ordering process with its consequent release of energy was proceeding more than fast enough to produce this rate of rise of temperature. It should be noticed that the relaxation

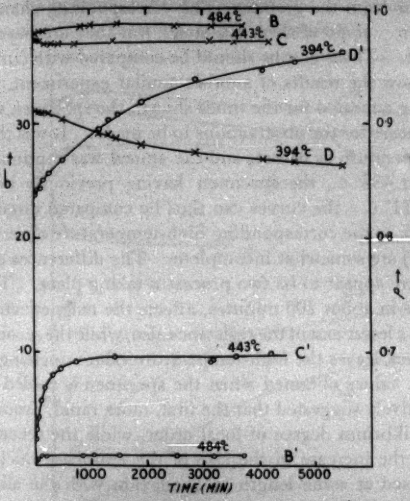

Figure 6.

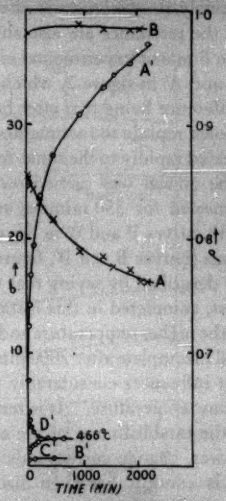

Figure 7.

Figure 6. Relaxation towards equilibrium. ×, resistance measurements; ○, magnetization measurements; B, B′, anneal at 484° c., previously at 517° c.; C, C′, anneal at 443° c., previously at 484° c.; D, D′, anneal at 394° c., previously at 443° c.

Figure 7. Relaxation towards equilibrium. ×, resistance measurements; ○, magnetization measurements; A, A′, anneal at 488° c., previously at 521° c., but quenched to room temperature at intervals, and measurements made there. B, B′, as above, but measurements made at 488° c. just prior to each quench; C′, D′, anneal at 466° c., the former previously at 488° c., and the latter previously at 437° c. The final value is the same in both cases, showing that it is the true equilibrium value corresponding to 466° c.

towards order, as marked by the point at which the specific heats of the quenched and annealed alloys begin to diverge, becomes appreciable in this experiment about 250° c.

We proceed now to describe some observations made on alloys not in equilibrium which, while unfortunately not as straightforward as was anticipated

* These measurements were kindly made by Dr F. W. Jones, of Metropolitan Vickers Electrical Co., Ltd., to whom I am also indebted for much valuable discussion of the work described in this paper.

when they were begun, are nevertheless of some interest. The first group of experiments was carried out as follows. The alloy was first obtained in an equilibrium state by prolonged annealing at constant temperature, and the temperature was then suddenly changed by twenty degrees or so. Observations were made both of resistance and magnetization while the new equilibrium was being attained. Some typical curves are shown in figure 6. The variation of σ with time is not, as it might appear to be, exponential, and there is no simple method of comparing the rates of relaxation at different temperatures ; qualitatively the variation is obvious from the graphs. The corresponding changes in the resistance are also shown ; some of them are small, but they are beyond the limits of experimental error. These graphs should be compared with curves A and A′ in figure 7, which show the results of another similar experiment, the difference being that after being annealed for the times shown, the specimen was cooled rapidly to room temperature for the observations to be made. It was then heated rapidly to the same temperature as before, and the anneal was continued. The anneal was carried out at 488° C., the specimen having previously been annealed for 350 minutes at 521° C.: the curves can thus be compared directly with curves B and B′ in figure 6, as the corresponding high-temperature observations (curves B and B′, figure 7) are somewhat incomplete. The differences can be described by saying that there appear to be two processes taking place. The first, completed in this instance in about 200 minutes, affects the magnetization at the higher temperature and to a lesser extent the resistance also, while the second, still incomplete after 2000 minutes, leaves the high-temperature values unchanged but influences considerably the values obtained when the specimen is cooled to room temperature. It is tentatively suggested that the first, more rapid, process is the establishment of the equilibrium degree of local order, while the second, slower, change corresponds to the increase in the size of the antiphase nuclei. This concept has been discussed at some length in connexion with the alloy Cu_3Au [2], [4], [5], and as this substance has the same structure as Ni_3Mn there is good antecedent reason for expecting the same phenomenon here also.

Before discussing this hypothesis further, however, it will be convenient to describe other experiments which throw some light on the question. The alloy was held for about half an hour at 600° C., so that it would be almost completely disordered. The temperature was then quickly reduced to 423° C., i.e. below the Curie point, and the resultant changes of magnetization and resistance were noted. Curves A and A′ in figure 8 show the results, the most striking features of which are the marked inflexion on the {σ, time} curve and the initial rise of the resistance before its ultimate slow fall. The same change—from 600° C. to 423° C.—was next carried out in two stages. The temperature was lowered quickly from 600° C. to 495° C., which is below the order-disorder transformation but above the Curie point, and was held there for 1400 minutes. During this time there was no significant change in the (small) value of σ, and the resistance increased slightly; see figure 8, curves C and C′. Immediately after this the temperature

was lowered to 423°c. and the anneal proceeded as before (figure 8, curves B and B′). The inflexion on the $\{\sigma, t\}$ curve had now disappeared, and the initial rise in the resistance was smaller and lasted a much shorter time. Unfortunately results are not available to show the effect on the specimen of being annealed at 423° c. after having been in equilibrium at, say, 450° c., but curve E′ is an estimate, interpolated from the other data, of what the result would be. It compares reasonably with curve D′, which shows the effect on the specimen of being annealed at 423° c. after having been in fair equilibrium at 394° c. It is in any case sufficiently accurate to show that the change would take place much more quickly than those represented by curves A′ and B′ in figure 8.

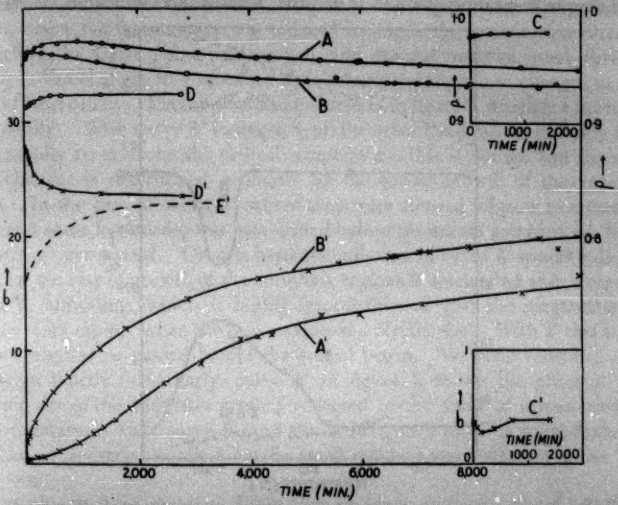

Figure 8. Anneal at 423° c. ⊙, resistance measurements; ×, magnetization measurements; A, A′, previously at 600° c.; B, B′, previously at 495° c. (see text); D, D′, previously at 394° c.; E′ previously at 450° c. (estimated curve).

The last experiment to be described consisted of quenching an alloy from equilibrium at 575° c., and observing the resistance and magnetization whilst reheating it at $1\frac{1}{2}$° c. per minute (figure 9, curves A and A′). This treatment corresponds exactly to that given to the specific-heat specimen when curve Q, figure 5, was obtained. The heating was interrupted at intervals, and the alloy was cooled rapidly to room temperature for resistance and magnetic measurements to be made; cf. figure 9, curves B and B′. The magnetization curve B′ shows quite clearly the onset of the ordering process at 260° c., reflected in the increasing value of σ, in agreement with the deductions from the specific-heat measurements. When the measurements are made at the higher temperatures, however, the

values of σ and therefore the changes in σ are much reduced, and, combined with the decrease always associated with increasing temperature, they fail to give rise to any singularity in curve A′ at this point. There is probably a slight rise about 410° c., corresponding to an accelerated increase in σ on curve B′. This may be due to (*a*) the increasing rate of relaxation with increasing temperature, (*b*) the attainment of some critical degree of local order, or, more probably, (*c*) some process connected with the growth of the antiphase nuclei. This point will be referred to again later. The corresponding room-temperature measurements of resistance, on the other hand, show no appreciable change until 400° c. has been passed, when a fall due to the increasing order takes place (figure 9, curve B). The simple re-heating curve A is of little help in this connexion, as its shape,

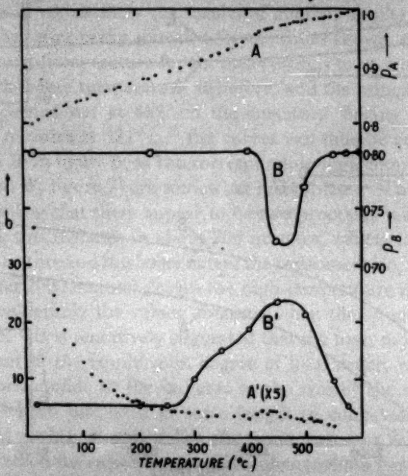

Figure 9. Reheating of quenched alloy. A, B, resistance measurements; A′, B′, magnetization measurements. Note that the vertical scale is increased by a factor of 5 for curve A′.

even in the absence of any changes of structure, appears to be complex, and it is not known. An experiment similar to ours, made by Valentiner and Becker[7], shows a sharp fall in the resistance about 460° c., but their account makes no mention of the rate of heating, which was presumably very slow.

§3. DISCUSSION OF RESULTS

In assessing the meaning of these results we will consider first curves A, B and A′, B′ in figure 8. It is impossible to make these pairs of curves coincide by any shift parallel to the time axis, and they must therefore correspond to different states of the alloy. But they were obtained from the same specimen at the same temperature, and the different states can, after appropriate annealing, give rise

to the same values of resistance or magnetization. From this it seems clear that these quantities, in so far as they are affected by the degree of order, cannot both be uniquely determined by one parameter only. The obvious suggestion is that both quantities depend, at least below the Curie point, on the degree of local order and also on the size of the antiphase regions. The two variables are not, of course, entirely independent. It is reasonable to suppose, as has indeed been shown by Sykes and Jones in the case of Cu_3Au, that the changes in local order proceed more easily, and therefore more rapidly and at a lower temperature, than the growth of the antiphase regions. The same workers have also shown that the best way to obtain a small number of large antiphase regions is by a long anneal just below the critical temperature. Thus in the experiments illustrated in figure 6, where the temperature was reduced in stages, the regions were already large before the Curie point was reached, and did not undergo much further alteration; the changes in σ recorded thus correspond mainly to changes in the degree of local order. This applies also to curve E′ in figure 8, which is a member of this family. With curve A′ in figure 8, on the other hand, where the alloy was cooled rapidly from above the critical temperature, this is not so, and the rate of the changes is determined primarily by the slower growth of the ordered regions. In the case of curve B′, where they were allowed to grow to a certain extent, and some local order was established before the anneal commenced, both quantities are concerned. On this basis the inflexion in curve A′ would indicate either that the rate of growth of the antiphase regions is accelerated after a certain amount of annealing, which is highly improbable, or that the magnetization increases more rapidly when the regions exceed a certain size. With B′ this stage has been reached or passed before the anneal began. We shall return to this point again shortly. Similarly, curve A′ in figure 7 shows the effect of the increasing size of the antiphase regions reflected in the value of σ measured at room temperature, while curve B′ (and also B′ in figure 6 and C′ in figure 8) shows that it has no appreciable effect on the small residual magnetization above the Curie point.

It has already been mentioned that changes in the state of order of any kind have little effect on the resistance at temperatures above the Curie point, although the resistance obtained on quenching to room temperatures is considerably altered. It is to be expected that the resistance will be affected both by the degree of local order and by the size of the ordered regions when this is comparable with the electronic mean free path. It has already been pointed out that both variables do seem to affect the resistance below the Curie point. We can now understand why in curve B in figure 9 the resistance remains unaltered up to 400° c. Although the local order has been increasing since 250° c., the ordered regions will still be small and long-distance order almost absent. When some of the regions grow at the expense of the others the resistance will fall, only to rise again shortly afterwards, owing mainly to the transition to the paramagnetic state. It is perhaps significant that this drop in the resistance occurs at the same point

as the accelerated rise in the magnetization (figure 9, curve B'). This would suggest that the more rapid increase in the magnetization is indeed connected with the attainment of some critical size of the antiphase regions, as has been already suggested in explanation of the point of inflexion in the annealing curve (figure 8, curve A'). This is a matter which might well repay further investigation.

The only other feature of the results calling for comment is the initial rise in the resistance, which appears in all cases to occur at the beginning of the transition from complete disorder towards order; see, for example, figure 6, curve B, and figure 8, curves A, B, and C. A similar behaviour has been previously recorded by Dahl (1), who, in the course of experiments on the effect of cold work, recorded also the changes in resistance accompanying the annealing of a quenched specimen. His results are in agreement with ours in so far as they can be compared. A comparison of our curves A and B, figure 8, in the light of the hypothesis outlined above, suggests that the rise is to be associated with the growth of the ordered regions. It might be suggested that it is due to some kind of strain resistance produced by this process were it not for the fact that no difference can be detected by X-ray methods between the ordered and disordered states in respect of either structure or lattice parameter. The effect can be observed above the Curie point; in fact, it is the only change produced by annealing at these temperatures (figure 6, curve B, and figure 8, curve C), and this fact discounts the alternative suggestion of an internal magneto-resistance effect.

§4. ACKNOWLEDGEMENTS

My best thanks are due to the Colston Research Society of the University of Bristol for financial assistance towards this work, and to Dr A. P. M. Fleming, Director of Research and Education Departments, Metropolitan Vickers Electrical Co., Ltd., in whose department the specific-heat measurements were made.

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MOLECULAR STRUCTURE FACTORS AND THEIR APPLICATION TO THE SOLUTION OF THE STRUCTURES OF COMPLEX ORGANIC CRYSTALS

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ABSTRACT. The transforms of some simple molecules are derived and their application to the solution of crystal structures is indicated by an example (naphthalene). The transform of a complex molecule can be built up from the transforms of its component parts, and it is suggested that the method provides another approach to the problem of the solution of the structure of complex organic crystals.

§ 1. INTRODUCTION

The trial-and-error solution of the structure of a complex organic crystal is usually a matter of considerable difficulty. Even though useful information may be provided by optical and magnetic data, it is no easy matter to find the orientation of the molecules in the unit cell, and the calculations involved are tedious and slow. At the same time the shape and dimensions of the molecule can often be inferred with some certainty. The same group of atoms may occur in many compounds, and even when the shape of the whole molecule is in doubt the shape and dimensions of some part or parts of it may be well known. For example, the six atoms in the configuration of a benzene ring form a constituent part of the molecules of a large number of organic compounds. It would appear desirable, therefore, to deduce for an assemblage of atoms of known shape a molecular scattering factor analogous to an atomic scattering factor. In this way we can treat the molecule as a unit with a characteristic scattering power for X rays, and reduce the problem to a solution of five parameters—three of translation of any point in the molecule, and two of rotation about two perpendicular axes intersecting in that point. The object of this paper is to show how such molecular structure factors, or Fourier transforms, can be calculated easily for certain examples, and how they can be used to simplify the solution of a complex structure.

§ 2. THE FOURIER TRANSFORM OF AN ORGANIC MOLECULE

The atomic structure of a crystal can be represented by a reciprocal lattice, every point of which is weighted with the structure factor of the plane corresponding to that point (1). In exactly the same way a molecule can be represented

by weighted reciprocal space[2]. Such a representation is termed the *Fourier transform* of the molecule.

The structure factor of any plane (hkl) in a crystal is given by

$$F_{hkl}=\Sigma f_{hkl}e^{2\pi i(hx/a+ky/b+lz/c)},$$

where a, b and c are the translations of the crystal lattice, x, y and z the atomic coordinates, and f_{hkl} is the atomic scattering factor for the angle of scattering corresponding to that plane. The summation is taken over all the atoms in the unit cell. If the crystal lattice is taken as orthorhombic, F_{hkl} may be written in terms of the reciprocal distances a^*, b^*, c^*, where $a^*=1/a$, $b^*=1/b$, $c^*=1/c$, if

$$F_{hkl}=\Sigma_{hkl}fe^{2\pi i(hxa^*+kyb^*+lz^*)}.$$

F_{hkl} is the weight in reciprocal space which is defined by the translations a^*, b^* and c^* of the reciprocal lattice. If F_{hkl} is calculated for all possible values of a^*, b^* and c^*, and if the structure factors so obtained are attached to their corresponding reciprocal points, we shall have a representation of the molecule as a continuous distribution of structure factor in reciprocal space.

The idealized transform. The Fourier transform is considerably simplified by omitting the atomic scattering factor, and this is permissible when the molecule is composed of one kind of atom only.† This idealized transform is that which would be derived from a molecule composed of point-like atoms, and it possesses certain repeat properties and symmetry not shown by the true Fourier transform. In order to revert to the latter, it is only necessary to multiply the idealized transform by the factor showing the falling off of atomic scattering with increasing angle of reflection.

The transform of the benzene ring. For the purposes of calculation a benzene ring is assumed to be a plane hexagon of side 1·4 A., and the transform is calculated for orthogonal axes. The atomic coordinates are

x	y	z
0·00	+1·40	0·00
0·00	−1·40	0·00
+1·21	+0·70	0·00
+1·21	−0·70	0·00
−1·21	+0·70	0·00
−1·21	−0·70	0·00

The plane of the molecule is taken parallel to the X, Y plane of coordinates, and the centre of the molecule is at the origin. The symbol T_{hkl} will be used to designate the weight of any reciprocal point in the idealized transform, F_{hkl} being kept for the true structure factor when the atomic scattering coefficient is retained. Then

$$\begin{aligned}T_{hkl}&=2[\cos 2\pi y'b^*+\cos 2\pi(xa^*+yb^*)+\cos 2\pi(xa^*-yb^*)]\\&=2[\cos 2\pi y'b^*+2\cos 2\pi xa^*.\cos 2\pi yb^*]\\y&=0{\cdot}70\text{ A.},\quad y'=1{\cdot}40\text{ A.},\quad x=1{\cdot}21\text{ A.}\end{aligned}$$

† To a first approximation it is also permissible when the molecule contains oxygen and nitrogen in addition to carbon, since the atomic scattering factors for these three atoms are very nearly the same.

This is a convenient form for calculation. When $a^*=0$ or $1/x$, and when $b^*=0$ or $1/y$, then

$$\cos 2\pi x a^* = \cos 2\pi y b^* = \cos 2\pi y' b^* = 1$$

and $$T_{hkl}=6.$$

Further, since

$$\cos[2\pi x(1/x+a^*)]=\cos 2\pi x a^* \text{ etc.},$$

the pattern of the idealized transform repeats at distances 1/1·21, 1/0·70 along the directions X and Y respectively. Further, it is easy to see that there are reflection planes for $a^*=1/2{\cdot}42$ and $b^*=1/1{\cdot}40$. It is only necessary therefore to calculate T_{hkl} for a sufficient number of points within one quarter of the repeat unit, or *unit cell*, of the transform. Since this is a plane molecule

$$T_{hkl}=T_{hk0}$$

The transform as a whole has hexagonal symmetry, and one quarter of the hexagonal unit cell is shown in figure 1.

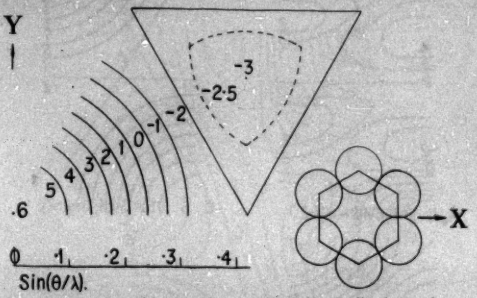

Figure 1. One quarter of the hexagonal unit cell of the idealized transform of benzene.

Several repeats of the transform are shown in figure 2.

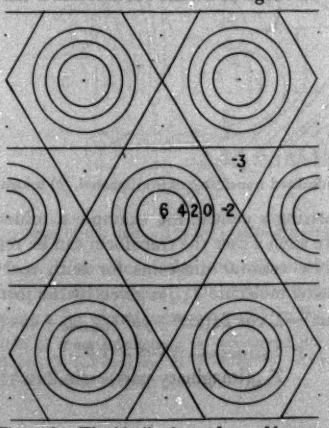

Figure 2. The idealized transform of benzene.

The contours in each case are drawn for every increment of 1 in T_{hkl}. From $+5$ to -1 the contours are very nearly circles, while for -2 they are straight lines intersecting at 60 degrees.

The side of the plane hexagon was assumed in the first place to be 1·40 A., but to obtain the transform for a plane hexagon of any size it is only necessary to change the scale of $\sin\theta/\lambda$. The true Fourier transform can be found from the idealized transform by introducing the atomic scattering factor. In this case

$$F_{hkl}=F_{hk0}\times\frac{f_{hkl}}{f_{hk0}}=T_{hk0}\times f_{hkl}.$$

The Fourier transforms of some benzene derivatives. A benzene ring has a centre of symmetry, and therefore T_{hkl} can be written as a sum of cosines. For

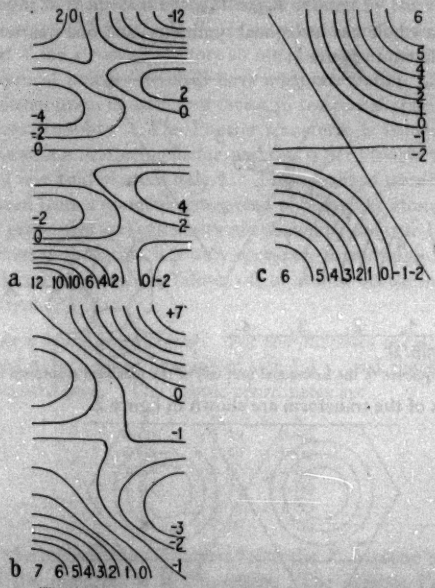

Figure 3. The idealized transforms of (*a*) diphenyl, (*b*) toluene and (*c*) benzene.

a molecule not possessing a centre, for example a toluene molecule, T_{hkl} is a complex quantity. In such a case the transform can be represented, graphically, only by giving separate contour diagrams for both real and imaginary parts. In the case of the toluene molecule T_{hkl} is given by the formula

$$T_{hkl}(\text{real part})=\Sigma\cos 2\pi(xa^*+yb^*)_{\text{benzene}}+\cos(2\pi y'b^*)_{\text{methyl}}$$
$$=T_{hkl\,(\text{benzene})}+\cos 2\pi y'b^*,$$

and

$$T_{hkl}(\text{imaginary part})=\sin 2\pi y'b^*.$$

The plane of the molecule is assumed to be parallel to the X, Y plane of coordinates, the centre of the ring is at the origin of coordinates, and the longest direction of the molecule is parallel to Y. The coordinates of the methyl atom are $0, y', 0$.

In diphenyl the molecule has two benzene rings whose centres are separated by a distance of $2y'$. If the centre of the molecule is taken as origin of coordinates, T_{hkl} can be written

$$\begin{aligned} T_{hkl\,(\text{diphenyl})} &= 2\Sigma \cos 2\pi[-xa^*+(y'-y)b^*] \\ &= 2\Sigma \cos 2\pi(xa^*+yb^*)\times\cos 2\pi y'b^* \\ &= 2T_{hkl\,(\text{benzene})}\times\cos 2\pi ky'b^*. \end{aligned}$$

$0, y', 0$ are the coordinates of the centre of a benzene ring, and x and y are the atomic coordinates referred to this centre as origin. Part of the transform of diphenyl is shown in figure 3 *a*, of toluene in figure 3 *b*, and of the equivalent area of benzene in figure 3 *c*.

Naphthalene.† The naphthalene molecule is assumed to be a plane double

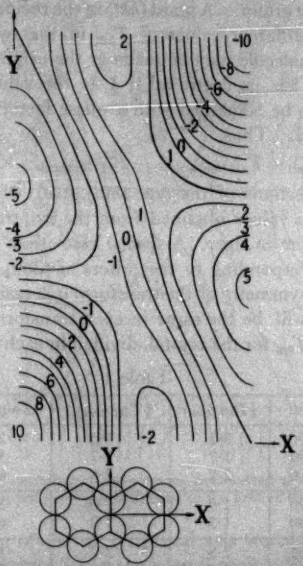

Figure 4. One quarter of the unit cell of the idealized transform of naphthalene.

hexagon of side 1·40 A. The size of the unit cell of the transform is the same as for benzene. One quarter of the unit cell of the transform is shown in figure 4, the contours being drawn for every increment of 1 in T_{hkl}.

† Since the completion of these calculations an account of the transform of anthracene has been given by A. Charlesby, G. I. Finch and H. Wilman [8]. As would be expected, the transforms of naphthalene and anthracene are very similar.

The derivation of the crystal structure of naphthalene on the basis of the molecular transform. The crystalline data, space group, etc., used in the following section are taken from the paper by J. M. Robertson[30]. The values of T_{hkl} for the crystal are obtained by dividing the experimental Fs given in that paper by their appropriate atomic scattering factors.

Naphthalene is monoclinic, of space group $P2_1/a$; its dimensions are as follows: $a=8{\cdot}29$ A., $b=5{\cdot}97$ A., $c=8{\cdot}68$ A., $\beta=122{\cdot}7°$. There are two molecules in the unit cell. The optics indicate that the long axes of the molecules are approximately parallel to one another and nearly parallel to the c crystallographic axis.

The weighted reciprocal lattice of the crystal, which is given by the experimental Fs, may be considered to be produced by the superposition of the Fourier transforms of the two molecules. If we choose any particular orientation for one molecule relative to the axes of the reciprocal lattice, the orientation of the other follows from the space group. A point (hkl) in the reciprocal lattice will in general correspond to two different values of T_{hkl} in the two molecular transforms. Further, since one molecule may be taken at the origin of the unit cell and the other molecule then has its centre at $\frac{1}{2}$, $\frac{1}{2}$, 0, the value of T_{hkl} for the second molecule will have to be combined with a phase factor of $+1$ or -1 according as $h+k$ is even or odd. Thus

$$T_{hkl\,(\text{crystal})}=T_{hkl\,(\text{molecule 1})}+T_{hkl\,(\text{molecule 2})}\times\cos\pi(h+k).$$

Clearly for those reflections of the type $(h0l)$, $(0k0)$ which are forbidden by the space group, the two values obtained from the two transforms will be equal in magnitude but opposite in sign. A special case arises for the point rows in the reciprocal lattice corresponding to the orders of (200), (020), (001). From the space group and the symmetry of the transform it is easily seen that the values of T_{hkl} for these points will be the same in each transform. Table 1 shows the values of T_{0k0}, T_{0k0}, T_{00l} for the crystal, divided in each case by two.

Table 1

hkl	$\frac{1}{2}T_{hkl}$ (obs.)	$\frac{1}{2}T_{hkl}$ (trans.)	2 sin (θ/λ)
200	5·3	5·6	·287
400	1·7	−1·7	·574
600	2·8	−2·6	·861
020	1·9	−2·0	·335
040	1·3	+1·2	·670
001	2·8	3·2	·134
002	2·0	−2·0	·269
003	2·9	2·4	·403
004	3·3	3·3	·537
005	0·7	−0·2	·672
006	1·2	−1·7	·773
007	1·9	−3·0	·940

From the seven orders of (001) we can find the orientation of the c^* reciprocal axis relative to the axes of the transform. We know from the optics that it must

lie near to the XY plane of coordinates and within a range of about 30° from X. If it lies in the XY plane the reciprocal points corresponding to these orders will be equally spaced along a line through the origin, at distances from the origin given by the fourth column of table 1. It will be seen from figure 5 that if it lies in the XY plane the c^* direction must make an angle of about 22° with X, if a fit between experimental and calculated values is to be obtained. The agreement is improved by inclining c^* to the XY plane. There does not appear to be any other direction for this line in the transform which gives good agreement between observed and calculated values. The third column in table 1, $\frac{1}{2}T_{h0l\,(\mathrm{trans.})}$, gives the values read off from the transform.

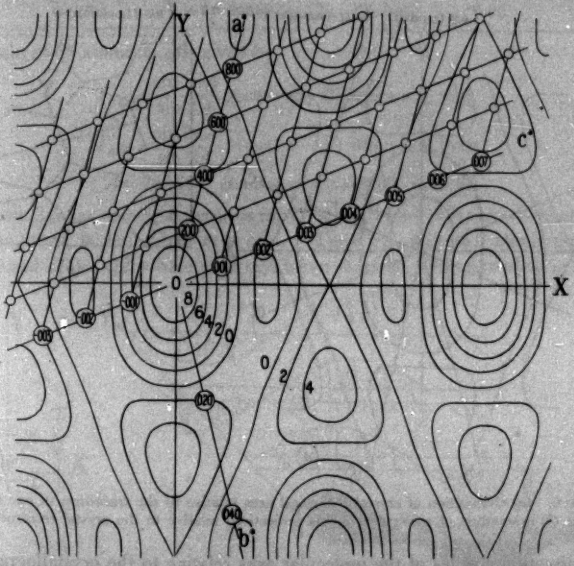

Figure 5. The transform of naphthalene showing the relationship of the crystal reciprocal axes and the reciprocal points of the ($h0l$) zone to the axes of the transform.

To find the orientation of the a^* reciprocal axis we can first put the point (200) on or near to the contour 5·3 in the central peak. If the distance of this point from the origin is a^*, then there must be points lying on the same line through the origin at distances $2a^*$, $3a^*$ which lie on or near to the contours 1·7 and 2·8 respectively. There appears to be only one direction for this line indicated in figure 5 by Oa^*. The direction of Ob^* now follows from the first two, and it will be seen that the points (020), (040) lie on contours giving values quite close to those experimentally obtained.

From the space group it will be seen that the molecules are parallel in the b-axis projection. The reciprocal points for the ($h0l$) zone can therefore be projected into the transform, and the values (and signs) for T_{h0l} (crystal) can be read off. In the a-axis and c-axis projections the molecules are not parallel and therefore T_{0kl} and T_{hk0} result from the combination of the different values obtained from each transform. Thus in figure 6, Oc_1^*, Ob_1^* are the projections of the reciprocal axes relative to the axes of the transform of one molecule. Then Oc_2^*, Ob_2^* are the projections of the reciprocal axes relative to the second molecule. These are, however, equivalent to $-Oc_1^*$ and Ob_1^* respectively. Thus the value of T_{0kl} for the crystal is given by

$$T_{0kl\,(\text{crystal})} = T_{0kl\,(\text{molecule})} + \cos \pi k \times T_{0k-l\,(\text{molecule})}.$$

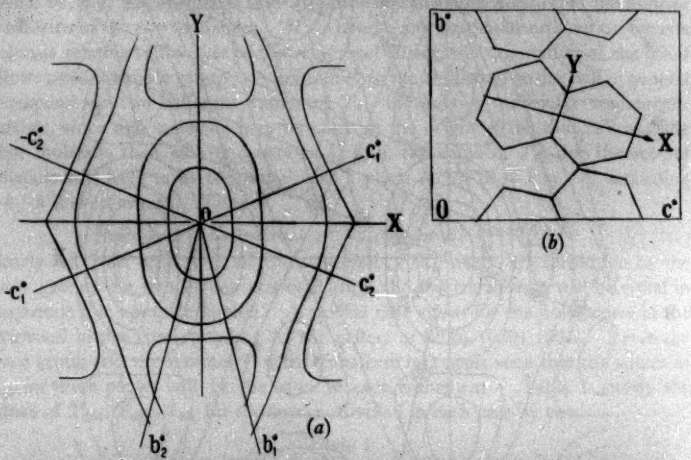

Figure 6. (*a*) Orientation of crystal reciprocal axes relative to the transform of one molecule; and (*b*) orientation of molecules (a-axis projection) relative to the crystal reciprocal axes.

The direction cosines of the molecular axes relative to the crystallographic axes are given in table 2, and those obtained by Robertson [3] are given for comparison.

Table 2

Author's values				Robertson's values			
	a	b	c^*		a	b	c^*
X	−·41	−·24	·88	X	−·428	−·219	·877
Y	·28	·89	·36	Y	·323	·876	·357

The signs of the Fourier components can be read off from the transform and the structure can be refined in the usual way.

§3. THE TRANSFORM OF AN ALIPHATIC CHAIN

For the purpose of calculation an aliphatic chain is assumed to be a plane zig-zag with an atom-to-atom distance of 1·54 A. and a bond angle of 109° 27′. The plane of the zig-zag is taken a the XY plane of coordinates and the origin is taken at the centre of the chain. The greatest length of the molecule is parallel to Y. The atomic coordinates are then

Atom	X	Y	Z
1	·89	·63	0·00
2	−·89	3×·63	0·00
•	•	•	•
n	$-(-1)^n\times 0{\cdot}89$	$(2n-1)\times 0{\cdot}63$	0·00

For a chain of $2n$ atoms T_{hkl} is given by

$$T_{hkl}=\frac{\sin 2nA}{\sin 2A}\times\cos(A+B) \text{ when } n \text{ is odd}$$

$$T_{hkl}=\frac{\sin 2nA}{\sin 2A}\times\cos(A-B) \text{ when } n \text{ is even.}$$

$$A=2\pi ky b^*,\ B=2\pi hx a^*,\ x=0{\cdot}89,\ y=0{\cdot}63.$$

$\sin 2nA/\sin 2A$ has principal maxima for $2A=m\pi$, where m is any whole number; $\cos A$, however, is zero when m is odd. Thus T_{0k0} will be a maximum when $2A=m\pi$ and $B=m'\pi/2$, where m' is odd when m is odd, and even when m is even.

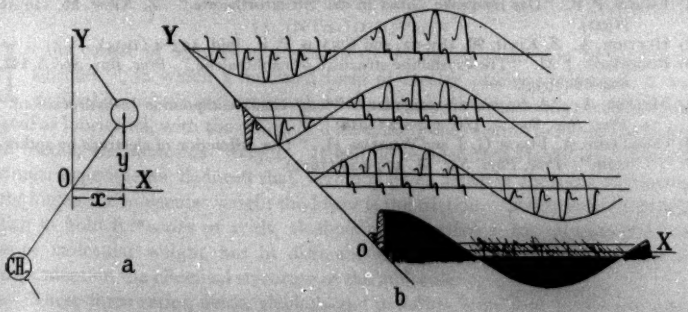

Figure 7. Diagrammatic representation of idealized transform of an aliphatic chain.

There will be secondary maxima for $2nA=(2p+1)\pi/2$. The magnitude of a principal maximum is $2n$ and that of the first secondary maximum is $2n/3\pi$, or roughly 1/10 of the value of the principal maximum. The width of a principal peak in the transform will be $1/2ny$. It will be noticed that the positions of the principal peaks in the transform are independent of the number of carbon atoms in the chain.

The X-ray reflections of $C_{29}H_{60}$. The crystals of $C_{29}H_{60}$ are orthorhombic, of space group P_{nam}; its dimensions are as follows: a=7·45 A., b=4·97 A.,

c=77·2 A. There are four molecules in the unit cell. T_{hkl} must be split into its real and imaginary parts when

$$T_{hkl\,(\text{real part})}=\frac{\sin 28A}{\sin 2A}\times\cos(A-B)+\cos(29A+B)$$

$$T_{hkl\,(\text{imaginary})}=\sin(29A+B).$$

The long axes of the molecules are parallel to c. Thus if a plane (00l) reflects x rays strongly, the reciprocal point corresponding to that plane must lie on a principal peak in the transform. These occur along the Y axis of the transform at distances given by $b^*=m/2y=m\times 0{\cdot}79$. Now $1/c$ for the crystal is 0·013, thus for (00l) to be a strong reflection $l/c=m\times 0{\cdot}79$, giving l=61 when m=1. The width of a principal peak is 0·035. Hence the reciprocal points corresponding to (001), ((0.0.60), (0.0.61), (0.0.62) will fall on principal peaks, and the reflections from these planes should be strong. Reflections of the type (hkl) should be strong for certain values of h and k when l=0, 1, 30, 31, 60, 61, 62, and in fact all other reflections are very weak or absent altogether (loc. cit.).

§ 5. ACKNOWLEDGEMENTS

The author is indebted to Dr. W. A. Wooster and Professor P. P. Ewald for their most helpful criticism and advice during the writing of this paper.

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A NOTE ON THE MECHANISM OF BOUNDARY LUBRICATION SUGGESTED BY THE STATIC FRICTION OF ESTERS

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Communicated by C. G. Darwin, F.R.S., 6 October 1939

ABSTRACT. The note gives the results of static-friction measurements of steel surfaces lubricated with series of methyl and ethyl esters. The series of ethyl esters was chosen to obtain a relation between coefficient of friction and molecular weight and an unexpected feature of the relation obtained is a maximum value of the coefficient of friction at a molecular weight of about 120.

A suggested explanation of this phenomenon is given by making certain assumptions regarding the structure and method of attachment of the molecules to the surface.

On the basis of these assumptions, the behaviour of a series of methyl esters was predicted before making tests, and the results of the tests subsequently carried out agree with the forecast.

§1. INTRODUCTION

In the course of a series of experiments on the static friction of lubricated surfaces [1], in which a modified form of Deeley machine was used, it was decided to include various members of a chemical series among the substances used as lubricants, with the object of determining the relation between coefficient of friction and molecular weight. It will be recalled that Hardy, as a result of similar experiments, deduced that, with any given series of chemical substances, the higher the molecular weight the lower is the friction. Hardy found this relation to hold for series of acids, alcohols and paraffins ; for substances of the same molecular weight but in different series the friction was found to be dependent on the chemical structure of the molecule.

These three series, acids, alcohols and paraffins, were first considered when the choice of a series suitable for the present experiments arose. Acids were ruled out because of previous experience of their chemical activity on steel surfaces ; for instance, in measurements of kinetic friction with steel surfaces lubricated with palmitic acid, the friction was very high and the surfaces were seriously attacked. Attempts were made to obtain series of paraffins and alcohols, but neither series, in a form sufficiently comprehensive for the purpose, could be secured at reasonable cost.

After some consideration it was decided to use a series of ethyl esters. A comprehensive series could be obtained easily, and the inactivity of esters from

a chemical point of view made the series suitable as regards freedom from surface corrosion. It was realized that the substitution of a C_2H_5 group for a hydrogen atom at the active end of the acid molecules might render the molecules inactive and prevent the desirable orientation of the molecules on the surfaces, but since Hardy obtained the friction–molecular weight relation for paraffins, which have no active end, there appeared to be no reason why esters should not behave similarly.

§ 2. FRICTION OF ETHYL ESTERS

Measurements were made of the static coefficient of friction of steel surfaces at air temperature when the surfaces were wetted with each of the following esters:—

Ester	Formula
Ethyl formate	$H.CO.O.C_2H_5$
Ethyl acetate	$CH_3.CO.O.C_2H_5$
Ethyl propionate	$C_2H_5.CO.O.C_2H_5$
Ethyl valerate	$C_4H_9.CO.O.C_2H_5$
Ethyl oenanthate	$C_6H_{13}.CO.O.C_2H_5$
Ethyl capryllate	$C_7H_{15}.CO.O.C_2H_5$
Ethyl pelargonate	$C_8H_{17}.CO.O.C_2H_5$
Ethyl laurate	$C_{11}H_{23}.CO.O.C_2H_5$
Ethyl palmitate	$C_{15}H_{31}.CO.O.C_2H_5$
Ethyl stearate	$C_{17}H_{35}.CO.O.C_2H_5$

It will be noted that the highest member of this series has a molecular weight more than four times that of the lowest member; ethyl palmitate and ethyl stearate have molecular weights greater than that of palmitic acid, which, according to Hardy, gave zero friction.

The surfaces were cleaned between tests by a procedure [1] developed at the commencement of the static-friction measurements, and measurements of the friction of steel on steel were made at each change as a check on the cleanliness of the surfaces [1].

§ 3. RESULTS

About seven or eight observations were made with each substance, and mean values are given in table 1. The variation from the mean was never greater than about 0·02.

Table 1

Ester	Molecular weight	Coefficient of friction
Ethyl formate	74	0·25
Ethyl acetate	88	0·27$_5$
Ethyl propionate	102	0·30
Ethyl valerate	130	0·31
Ethyl oenanthate	158	0·27
Ethyl capryllate	172	0·23
Ethyl pelargonate	186	0·23
Ethyl laurate	228	0·18
Ethyl palmitate	284	0·17
Ethyl stearate	312	0·17

The results are plotted, coefficient of friction against molecular weight, in figure 1. It will be seen that, from a molecular weight of about 130 and upwards, the coefficient of friction decreases with increase of molecular weight, but not linearly, as was stated by Hardy for paraffins, alcohols and acids.

The most striking feature of the results, however, is the maximum value of the coefficient of friction recorded at a molecular weight of about 120, the friction decreasing at lower as well as at higher molecular weights.

Errors in observation or inefficient cleaning of the surface were suspected in the case of the three lower esters, although all the tests had been carried out in apparently the same manner, and the mean of several observations had been

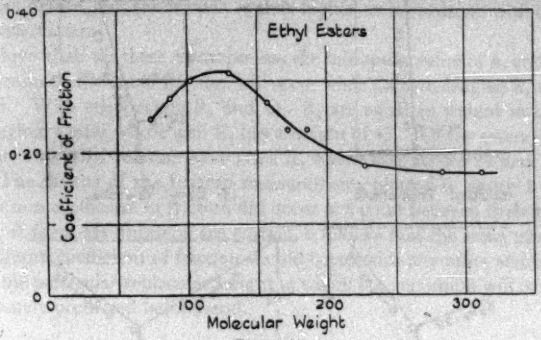

Figure 1.

taken. All the observations for the complete series were repeated with fresh samples of the esters, and an identical curve was obtained. The maximum value of the coefficient of friction, therefore, appears to be a characteristic of this series of esters at least.

In order to explain this difference between the relation between friction and molecular weight in the ethyl esters and the corresponding relation in the acids, alcohols and paraffins (which, according to Hardy, give a uniform relation throughout the whole range of molecular weight), the following suggestions are made regarding the nature of the boundary film. The general structural formula for an ester may be written

$$R_1-C\begin{matrix}=O\\ \diagdown O-R_2'\end{matrix}$$

R_1 and R_2 being the acid and alcohol radicals.

In this case R_1 is C_nH_{2n+1}, for values 0, 1, 2, 4, 6, 7, 8, 11, 15 and 17 of n, and R_2 is C_2H_5.

If it is assumed that the ester molecule attaches itself to the metal surface by means of the double-bond oxygen atom, there will then be projecting from the

surface, firstly, a fractional length of the molecule, O=C, and, secondly, from this point, two diverging projections R_1 and $O-R_2$; that is, the molecule will stand on the surface like a tree with two branches. Now, assuming that the length of each of these branches is proportional to the fractional molecular weight of the arms R_1 and $O-R_2$, and that there is flexibility at the junction of the molecule and the surface (or in the molecule itself at the junction of the arms R_1 and $O-R_2$), then the molecules of the first five ethyl esters tested as attached to the metal surface may be represented by the diagrams (*a*) to (*e*), figure 2.

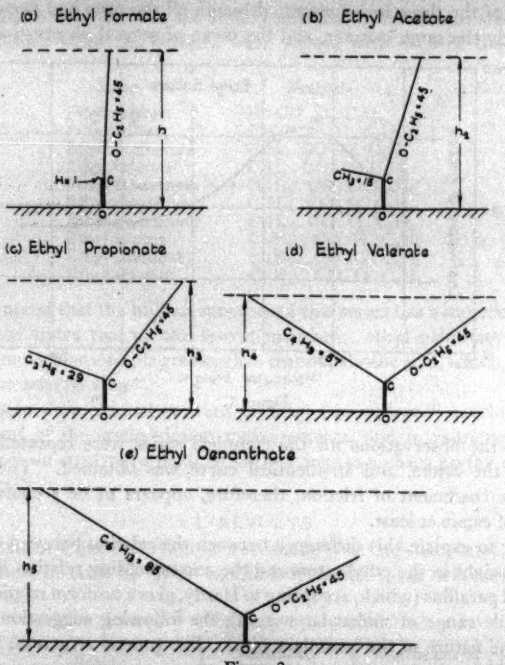

Figure 2.

The distance of the central carbon atom from the surface is not intended to be representative of the fractional molecular weight of this part of the molecule, since it is constant in all five cases. The two atoms O and C are shown close together so that the issue is substantially the same whether flexibility is about the surface, i.e. about the atom O, or is in the molecule at atom C.

In diagram (*a*) the molecule is ethyl formate. The arm-lengths are proportional to 1 and 45, the weights of R_1 and $O-R_2$. Because of the much greater weight of the arm $O-R_2$ as against that of the arm R_1, the molecule is shown with

the arm $O-R_2$ almost perpendicular to the surface. The distance from the surface to the tip of the molecule is given by h_1, and the coefficient of friction—based on the attractive forces between opposing surfaces—is then inversely proportional to some power of h_1.

In diagram (*b*) the molecule is ethyl acetate. The length of one arm is the same as in diagram (*a*), but the other is now much larger than it previously was (its weight is now 15 as against 1), and this circumstance plays a more powerful part in the final positioning of the whole molecule. The result is that the arm $O-C_2H_5$ (weight 45) is further removed from the perpendicular to the surface than in diagram (*a*), the distance h_2 of the tip of the molecule from the surface is less than before, and the friction is thus higher, in accordance with the experimental observations.

It follows that, on these assumptions, the minimum value of h, and therefore the maximum coefficient of friction, will occur when the arm-lengths R_1 and $O-R_2$ are equal. With ethyl esters R_1 and $O-R_2$ are equal in weight in the case of some imaginary ester whose arm R_1 has a weight of 45. Of the esters used, ethyl propionate and ethyl valerate have arms R_1 whose weights are 29 and 57 respectively. The results of the friction measurements plotted in figure 1 show that the maximum coefficient of friction did occur at a point between these two esters.

Now, if these assumptions are correct, it follows that the same phenomenon of a maximum coefficient of friction should occur with any other series of esters, and that the particular molecular weight at which the maximum will occur can be approximately predicted beforehand.

§ 4. METHYL ESTERS

In the case of methyl esters, for instance, the arm $O-R_2$ has a weight of 31 ($O-CH_3$). The first five members of the methyl series are given in table 2 with the structural formulae and the weights of the whole and parts of the molecules.

Table 2

Ester	Structural formula	Whole molecule	Weight of arm R_2	Weight of arm $O-R_2$
Methyl formate	$H-C(=O)-O-CH_3$	60	1	31
Methyl acetate	$CH_3-C(=O)-O-CH_3$	74	15	31
Methyl propionate	$C_2H_5-C(=O)-O-CH_3$	88	29	31
Methyl butyrate	$C_3H_7-C(=O)-O-CH_3$	102	43	31
Methyl valerate	$C_4H_9-C(=O)-O-CH_3$	116	57	31

From table 2 it is seen that methyl propionate is the ester which comes nearest to having its arms R_1 and $O-R_2$ equal in weight. The maximum value of coefficient of friction should therefore occur at a molecular weight of approximately 88.

§5. RESULTS WITH METHYL ESTERS

Observations of the coefficient of friction were made with the surfaces wetted with each of the above five substances, the usual cleaning process and the steel-on-steel tests being carried out between each set of observations. The mean values of several observations on each substance are given in table 3 and plotted in figure 3.

Table 3.

Ester	Molecular weight	Coefficient of friction
Methyl formate	60	$0{\cdot}28_5$
Methyl acetate	74	$0{\cdot}30_5$
Methyl propionate	88	0·32
Methyl butyrate	102	0·28
Methyl valerate	116	0·25

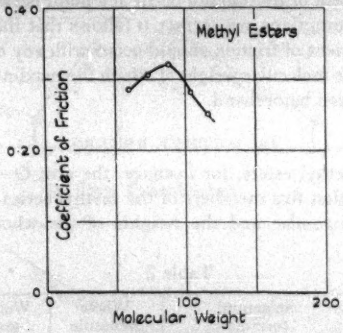

Figure 3.

The curve in figure 3 is similar to the one obtained for ethyl esters, and the maximum coefficient of friction occurs, as was predicted, at a molecular weight of approximately 90, the nearest ester being methyl propionate.

A comparison of the results obtained for the two series, methyl esters and ethyl esters, shows that the maximum value of the coefficient of friction is slightly higher for the methyl series than for the ethyl series. This is to be expected if the maximum occurs in each case when the arms R_1 and $O-R_2$ are equal, since, with this condition, the arms of the methyl ester are lighter and therefore shorter than the arms of the ethyl ester ; the tip of the methyl-ester molecule is therefore at a smaller distance from the surface, and the friction is thus higher.

§6. CONCLUSION

The relation between coefficient of friction and molecular weight for methyl and ethyl esters indicates that (1) the molecules in the boundary layer are attached to the surface by means of the double-bond oxygen atom in the general formula

$$R_1-C\overset{O}{\diagdown\!\!\diagup}O-R_2;$$

(2) each molecule has two divergent arms projecting from the surface; and (3) the orientation of these parts of the molecule relative to the surface varies with molecular weight and is dependent on the relative weights of the arms. The change in orientation may take place where the molecule is attached to the surface, or it may result from flexibility in the molecule.

§7. ACKNOWLEDGEMENTS

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THE USE OF CALCULATING MACHINES IN RAY TRACING

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Read 20 *April* 1939

Some while ago Dr. L. C. Martin sought my advice on the most suitable calculating machine for use in teaching optics. Although I do not claim any knowledge of optics, I found the adaptation of simple ray-tracing to mechanical computation an interesting study, and I give here such judgments as I have been able to form.

In the first place it appears that the greater portion of the computing time will be spent in consulting tables—so much so that more saving can be achieved by a suitable choice of tables than by using an electric calculating machine instead of a hand one.

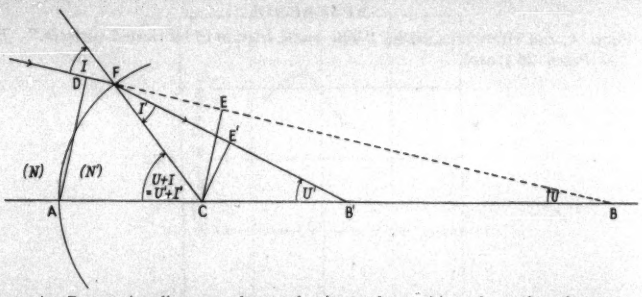

Figure 1. Ray-tracing diagram. Accented points and quantities refer to the refracted ray.

Figure 1 shows the standard ray-tracing diagram, with the notation and conventions of Conrady's excellent *Applied Optics and Optical Design*. If P is the perpendicular AD, d is the axial distance between refracting surfaces, and L=AB, the standard formulæ may be rewritten:

$$\sin I = \frac{P}{r} - \sin U \tag{1}$$

$$\sin I' = \frac{N}{N'} \sin I \tag{2}$$

$$U' = U + I - I' \tag{3}$$

$$L' = r\frac{(\sin I' + \sin U')}{\sin U'} \tag{4}$$

$$\left.\begin{aligned} P' &= L' \sin U' \\ &= r(\sin I' + \sin U') \end{aligned}\right\} \quad (5)$$

$$P \text{ (for new surface)} = P' - d \sin U' \quad (6)$$

In the proposed formulæ we may isolate the quantities that are independent of P and U, i.e. r, N and d. Thus for a ray travelling from air and reaching air again through n surfaces:

$$\begin{array}{lll} A_1 = \dfrac{1}{r_1} & B_1 = \dfrac{L_1 - r_1}{r_1} & C_1 = \dfrac{1}{N_1} \\ A_2 = \dfrac{r_1}{r_2} & B_2 = \dfrac{r_1 - d_1 - r_2}{r_2} & C_2 = \dfrac{N_1}{N_2} \\ \cdots & \cdots & \cdots \\ A_n = \dfrac{r_{n-1}}{r_n} & B_n = \dfrac{r_{n-1} - d_{n-1} - r_n}{r_n} & C_n = N_{n-1} \end{array}$$

Partial checks:

$$A_1 . A_2 . A_3 \ldots A_n . r_n = 1$$
$$\Sigma B r = L_1 - \Sigma d - r_n$$
$$C_1 . C_2 . C_3 \ldots C_n = 1$$

Then

$$\begin{aligned} U_1 &= U_1 \\ \sin I_1 &= B_1 \sin U_1 = A_1 P_1 - \sin U_1 \\ \sin I_1' &= C_1 \sin I_1 \\ U_2 &= U_1 + I_1 - I_1' \\ \sin I_2 &= A_2 \sin I_1' + B_2 \sin U_2 \\ \sin I_2' &= C_2 \sin I_2 \\ &\cdots \qquad \cdots \\ U_n &= U_{n-1} + I_{n-1} - I'_{n-1} \\ \sin I_n &= A_n \sin I'_{n-1} + B_n \sin U_n \\ \sin I_n' &= C_n \sin I_n \\ U_{n+1} &= U_n + I_n - I_n' \\ L_{n+1} &= r_n \frac{(\sin I_n' + \sin U_{n+1})}{\sin U_{n+1}} \end{aligned}$$

or $$P_{n+1} = r_n (\sin I_n' + \sin U_{n+1})$$

We revert now to the all-important question of tables. The desiderata are (*a*) a small interval, in order to reduce interpolation to a minimum and (*b*) a decimal system of angles, so that additions and subtractions may be done on the machine. Very few calculations require more than 6-figure tables, and many can be done with 5-figure tables. The smallest interval in any existing table of the natural values of the trigonometrical functions (with which alone we are

concerned) is 1″, as given in the badly-arranged and none too accurate 8-figure tables of Gifford * and in the new beautifully printed 8-figure tables of Peters. Although Peters' table could be used for exceptional cases, the sexagesimal system is unsuitable for general use. As the angles appear on paper only, any convenient system may be used.

The alternative systems are radians, degrees and decimals, and grades and decimals. Of the first-named there are no direct tables at a closer interval than $0^r{\cdot}001$ or 206″, which is too coarse. There are, however, excellent and most useful tables by Chrétien, giving differences between angles in radians and their sines; there is a 6-figure critical table (equivalent to working to 0″·2) up to 10°, and a 5-figure table (equivalent to working to 2″) up to 30°. This is the simplest of all 5-figure tables to use, and the fastest. A similar 6-figure table to 30°, with a 7-figure extension to 10°, would be most valuable.

In degrees and decimals there are the 5-figure tables of Lohse, and the 6-figure tables of Peters, both at interval 0°·01 or 36″, and the 7-figure table of Peters for every 0°·001 or 3″·6. A better selection is offered in grades, with the 5-figure tables of Steinbrenner for every $0^g{\cdot}01$ or 32″·4 and the new 6-figure tables of Peters at interval $0^g{\cdot}001$ or 3″·24. In both of these the maximum difference is 16, and it is not till 19^g that a difference as low as 14 can occur, so that the proportional parts for 15 and 16 are soon memorised, and can be applied mentally. The functions are divided with a final group of three figures, and so fit perfectly on to machines like the Brunsviga, Facit or Marchant, in which the keyboard is divided into groups of three figures. Our choice for 5-figure work is, therefore, Chrétien or Steinbrenner, with Peters ($0^g{\cdot}001$) for 6-figure work. In reserve we have Peters (7-figure, 0°·001), Roussilhe and Brandicourt (8-figure, $0^g{\cdot}01$) and Peters (8-figure, 1″).

The calculating scheme, together with its application with Chrétien's tables (the 6-figure portion) and with Peters', is shown below. The example is taken from Conrady, p. 47. The signs are written once only, as they obviously apply to both sine and angle.

$$L_1=-24 \quad r_1=10 \quad r_2=-5 \quad d_1=0{\cdot}6 \quad N=1{\cdot}518$$

		Chrétien		*Peters*	
Constants		Sine	△	Sine	Angle
$B_1-3{\cdot}4$	U_1-	17 452	1	69 756	4 44 44
C_1 0·658 762	I_1+	59 337	35	237 170	15 24 40
A_2-2	$I_1'+$	39 089	10	156 239	9 98 74
$B_2-2{\cdot}88$	U_2+	2 820	0	12 758	81 22
C_2 1·518	I_2-	86 300	107	349 221	22 71 07
	$I_2'-$	131 003	378	530 117	35 57 04
r_2-5	U_3+	47 776	18	213 110	13 67 19
	L_2	8·7101		7·4376	

* The full titles of these and other tables mentioned can be supplied by Scientific Computing Service Ltd., 23 Bedford Square, London, W.C. 1.

In the Chrétien example the angles are not written, since

$$U' = \sin U + \Delta(\sin U) + \sin I + \Delta(\sin I) - \sin I' - \Delta(\sin I')$$

$$\sin U' = U' - \Delta(U')$$

In adding to get U', each Δ is added with the same sign as its sine. When Δ is small it is added mentally to the sine; otherwise it is set separately. Thus the first settings could be 17 453, 59 372 and 39 099.

The Brunsviga models 15 and 20 have a device for transferring the contents of the product register to the setting levers. This is very valuable, not only in saving a great deal of setting (in the Chrétien calculation the machine is not cleared at all) but also as a means of converting complements to their direct form by transferring them to the levers and turning the handle backwards; the direct form can then be transferred for a subsequent multiplication.

In the logarithmic form of calculation there are five tabular entries for each surface, whereas in the machine form there are three entries only. The amount of writing in the machine form is less than half of that in the logarithmic form, while mental addition and subtraction are eliminated entirely if we express the angles in a decimal system. Thus from one-third to one-half of the work is eliminated. Apart from the saving in time, the mind is kept fresher for processes requiring thought and judgment.

The table below gives the approximate times (exclusive of checking) per surface with different tables.

Table	Working unit	Time (min.)
Conrady, 5-figure logarithms	1″	6–8
Lohse, 5-figure, interpolated	0°·001	3
Steinbrenner, 5-figure, interpolated	0ᵍ·001	3
Peters, 6-figure, not interpolated	0ᵍ·001	3
Chrétien, 5-figure, no interpolation	0ʳ·00001	2½
Chrétien, 6-figure, no interpolation	0ʳ·000001	3
Peters, 8-figure, no interpolation	1″	4
Peters, 6-figure, interpolated	0ᵍ·0001	4
Roussilhe and Brandicourt, 8-figure	0ᵍ·000001	8

The conclusions formed are that: (1) students of optics should be taught the use of calculating machines from the beginning of their course; (2) a hand machine, especially one with transfer from the product register to the setting levers, suffices for this work (an electric machine, costing twice as much, would not be justified for student use); (3) the choice of tables is as important as that of machines; a survey leads to the recommendation of Chrétien, Steinbrenner, and Peters; (4) it is not sufficient to use without examination the formulæ that have been developed for logarithmic work; the formulæ must be re-investigated to take full advantage of machine facilities and properties.

DISCUSSION

Dr. L. C. Martin. Some years ago considerable attention was given at the Imperial College to the question whether students of optical computing should be instructed to perform ray-tracing by logarithmic calculations or by the use of calculating machines. It was found that with the machines then available the preference had to be given to the first method, namely logarithmic work. The speed thus obtained could not be improved upon by the machine; moreover, the paper work records the computation step by step, a matter of especial importance in instructing students. Having regard to recent improvements in calculating machines, should this decision be revised?

Professor Conrady, who had carried out the tests I have mentioned, developed his methods of computation and design on the assumption that logarithmic reckoning would be employed for ray-tracing. The ray-tracing data obtained in the traditional way provide the quantities required for, *inter alia*, (*a*) a check calculation, which, in the case of a long radius, will give a result more accurate than the standard schedule, and will be employed to give the ray intersection distance to be transferred to the next surface; (*b*) a calculation of the difference in optical path between a marginal and a paraxial ray; (*c*) a calculation of the intercepts of the rays between the various surfaces, leading to the correction of chromatic aberrations in the physical sense, or (if carried out along a principal ray) to the investigation of the tangential and sagittal fans of rays.

The check calculation mentioned in (*a*) can be chosen so as to facilitate either (*b*) or (*c*).

Experience with the system so developed leaves little doubt that, whether worked logarithmically or not, it is a very powerful method of controlling the later stages of an optical calculation in the majority of cases. It is thus important to realize that the operation of ray-tracing is, at least in the later stages, the foundation for much supplementary calculation. It is definitely advantageous to use a method in which the lengths of ray intercepts between surfaces can be obtained as the work proceeds.

In deciding whether it would be an advantage to adopt machine methods of calculation, the subjects of the foregoing paragraphs would have to be brought into consideration even in discussing the method or methods for systematic working in ray-tracing. Naturally there are many other points which would present themselves in considering optical calculations in a wider sense.

Mr. J. W. Perry. Various sets of tables are now available and were mentioned by Dr. Comrie, proceeding by decimals of the quadrant. These are in some respects valuable additions to the computer's armoury, but it does not seem to me that of all possible tables with decimal subdivision of angle these have for our present purposes very much to recommend them beyond the fact that some such tables exist. It is true that a potential demand for such tables has been created by a recent decree elsewhere, and their supply in some variety is thus no doubt

stimulated, but their natural virtues are not thereby extended. These remain those of an arbitrary system.

Granted the advantage of decimalization, the only unit that appears to me to offer peculiar advantages for optical computations is the radian. In this unit Chrétien's tabulation is, I believe, the only really useful one available. It is to be hoped that others will follow to supplement and amplify this in scope and accuracy.

Where, as in the case of dioptric imagery, aberrations or similar functional deviations result from the difference or disproportionality between sine and arc, it is to be expected that in their computation the use of tables which give this difference directly and incidentally, will increase the amount of useful information obtainable from any specific calculation. This is actually the case, as may be seen from the following calculation of axial spherical aberration. In the angle transfer of the Seidel trace for the axial plane, sin U' is generally found from U' by tables. The procedure adopted to find U' may be expressed as follows:

$$U'=A+B$$

where

$$A=\sin U+\sin I-\sin I'$$

$$B=\ \Delta U+\Delta I-\Delta I'$$

$$\Delta x=\text{arc } x-\sin x$$

in the usual notation, x being here any variable. Now let

$$D=B-\Delta U'$$

Then the spherical-aberration increment for any given surface in terms of $\delta(nu \sin U.\delta L)$ is given by

$$\delta(nu \sin U.\delta L)=-hn \sin i.rD$$

This will be recognized as a well-known relation restated in a form convenient for calculation.

The quantities U, L and D here refer to the particular zonal ray in question, while u, h and i should be as given by the corresponding paraxial trace for which $\Delta x=0$. One may, however, ignore this distinction in order to obtain an approximation of some value, useful for the analysis of the aberrational correction, and obtainable with almost negligible additional calculation.

The choice of a particular form for ray-tracing is subject to appreciable individual preference, but any generally acceptable form would have to offer some facility for path-length calculation. This is necessary for the determination of path-differences and also in the calculation of the co-ordinates of spherical surfaces to fulfil given conditions. To exemplify the procedure in the latter case, consider the axial correction of a system by the modification of an external surface, S.

Let σ be the plane perpendicular to the optical axis x, and containing the vertex O of the refracting surface s. Let L and L' be the intersection distances from O of the incident and refracted rays proceeding at axial inclinations U and U'. Let the path-length for the incident ray prior to refraction, measured to its intersection $(0, Y)$ in σ, be Δ, relative to zero path-length for the corresponding point

(0, 0) for the paraxial ray. Then for the image at $(L', 0)$ to be free from aberration, the distance R along the incident ray from the point $(0, Y)$ to the intersection with the desired surface will be given by expressions of the form:

$$AR^2-BR+C=0$$

where $$A=\left(\frac{n}{n'}\right)^2-1$$

$$B=2\left[\left\{L'\left(\frac{n}{n'}-\cos u\right)-L\tan U\sin U\right\}-\frac{n}{n'}\left(\frac{\Delta}{n'}\right)\right]$$

$$C=\frac{\Delta}{n'}\left(\frac{\Delta}{n'}-2L'\right)-(L\tan U)^2$$

The co-ordinates (x, y) of the desired surface will then be $(R\cos U, Y-R\sin U)$ If $U=0$, R reduces to the simple form:

$$R=\frac{\Delta}{n'\cos U-n}$$

One may in this way also calculate, for example, what surface results from a deformation complying with an interferometric null test such as is made with the Hilger interferometer. The conditions of such a test need not, however, necessarily be those of the ultimate employment of the particular surface in question. For it is possible, by varying the conditions of the interferometer test in an appropriate way determined by calculation, to test the surface for its accuracy of approach to a form appropriate to aberrational correction under quite different conditions, including even those which cannot be reproduced, or are inconvenient of application in such tests. Such a modification in the conditions of test may affect the magnification of the system or entail some radical change in its construction. The ultimately intended conditions of application under which such a surface would provide the desired correction may be, for example, the performance in invisible light or a state of correction suitable for pairing with some other combination not immediately available. The working out of the appropriately modified conditions calls for routine calculation of the surface co-ordinates. Further data such as the tangent and curvature may be subsequently determined by subsidiary calculation.

THE HEATING OF THIN MOLYBDENUM FILMS IN A HIGH-FREQUENCY ELECTRIC FIELD

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ABSTRACT. Molybdenum films, formed by evaporation of molybdenum on to a glass substrate, are investigated by measurement of the heating which occurs on the application of a high-frequency electric field. The effects of varying glass temperature during deposition, and of contaminating the glass with oxygen, hydrogen, and with layers of metallic oxides or fluorides, are observed. The stability of the films is examined and related to the processes of agglomeration and recrystallization. The effect of bombarding the films with electrons is investigated.

§1. INTRODUCTION

THE object of this work was to determine the heating which occurs in thin films of molybdenum on the application of a high-frequency electric field. The films were deposited on the walls of a glass bulb by evaporation in high vacuum. With a field of constant frequency and intensity, it was desired to study the effect of varying film-thickness, and of varying the condition or nature of the surface on which the film was deposited. The results are of interest in two respects. Firstly, it sometimes happens in the manufacture of vacuum devices that metallic films are deposited on the non-conducting envelope; molybdenum is commonly employed in such devices and may be deposited by various mechanisms. In operation, high-frequency fields may be present, being created by the device or by a neighbouring circuit. It is therefore important to know under what conditions energy may be dissipated in the films, and whether such losses, if they occur, can be minimized. Secondly, since the high-frequency heating depends both on the electrical conductivity of the material of the film and on its structure, information is obtained concerning these two properties.

The field was applied by means of two electrodes external to the bulb, so as to avoid the need for contacts to the film which arises in investigating the electrical properties under d.c. conditions. The heating was studied by observation of the rise of temperature of the glass on application of the field. An observation thus represents an average behaviour over a considerable area of film.

The electrical properties of various types of thin film measured under d.c. conditions are described in the papers numbered (1) to (6) in the list of references

on page 265, while the structure is discussed in papers (7) to (14). Of these, papers (5), (6) and (14) refer to molybdenum. The present results are discussed as regards their relationship with certain of these papers.

§ 2. EXPERIMENTAL PROCEDURE

Pretreatment. A molybdenum wire was cleaned by flashing in "forming gas", consisting of 1 part of nitrogen to 3 of hydrogen, and was mounted in a bulb as shown in figure 1. The bulb was previously cleaned by being washed in dilute hydrochloric acid and distilled water, and was dried by a short air bake at 200° C. The bulb was evacuated to a pressure of about 10^{-7} mm., and was degassed by being heated in vacuo for at least half an hour, usually for several hours. The temperature was 400° C. in the case of lead glass, and 550° C. in the case of hard glass. The filament was then flashed in vacuo at 1900° K. for 20 minutes.

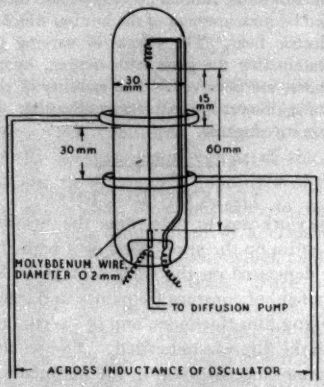

Figure 1. Apparatus.

Experiment. The glass temperature was adjusted at the required value by means of an oven, and the film was formed with the filament at 2150° K. Here the rate of evaporation is $6 \cdot 10^{-8}$ g./cm²-sec., compared with $1 \cdot 10^{-9}$ g./cm²-sec. at 1900° K. At intervals during the formation of the film the filament and glass were cooled to room temperature, and h.f. voltage was applied as shown in figure 1 for a standard period. The frequency was $3 \cdot 10^{7}$ c./sec. The geometry of the system was such that the rings gave a uniform field over the central region of the film. In the presence of a suitable film, heating of the glass occurred, and the temperature at the end of a run was determined by means of a strip thermocouple applied midway between the rings. The standard period was chosen sufficiently long (5 minutes) for temperature equilibrium with the surroundings to be obtained for various types of film. The highest temperature recorded after a run was 100° C., which would not produce any appreciable

irreversible effect in the film, as was shown by the work on the effect of temperature. Changes in resistivity during a run might, however, be appreciable.

Film thickness. The quantity of molybdenum deposited was estimated from the known evaporation rate of molybdenum given above, and also by a chemical method applied to the bulb after the completion of an experiment. The results of several estimations by this method were consistent and in good agreement with the accepted evaporation rates. The film was non-uniform in the direction of the filament owing to end-cooling, and because the film continued beyond the levels of the filament ends. On this account the estimation of quantity of molybdenum between the rings was not accurate; however, the error should be the same for all the experiments, and should not affect comparison between them. Values given for film thickness have a possible error of about 30 per cent on account of this non-uniformity.

The unit of thickness is taken throughout as that of a film which, if uniform, contains $2{\cdot}5 \cdot 10^{-7}$ g. of molybdenum per cm^2 If the film has the density of molybdenum in bulk, this unit is identical with the thickness of a single layer of molybdenum atoms. The unit is therefore described for convenience as "one atomic layer". The density of thin molybdenum films is, however, unknown, so that this term is entirely one of convenience.

Contaminating layers. When it was desired to evaporate a second substance on to the glass walls, a tungsten filament carrying a coating of this substance was mounted alongside the molybdenum filament. This filament could be heated by separate supply, and was also used, either uncoated or after a coating had been evaporated from it, as a cathode for the production of electrons in the tube. The molybdenum filament then formed an anode at a potential of 300 volts positive to the cathode. There were sufficient stray electrons to cause bombardment of the glass walls, as was verified by replacing the tungsten by an oxide cathode and coating the walls with fluorescent material. Bombardment was found to occur over the whole circumference of the bulb. This agrees with the results obtained by Afanasjewa[15], which indicate that the film could be regarded as bombarded by 300-volt electrons.

§ 3. DEPENDENCE OF HEATING ON RESISTANCE AND STRUCTURE

If the system of rings and film could be reduced as regards displacement current to an equivalent capacity C and as regards conduction current to a resistance R, then at frequency f the watts developed would have a maximum value when $R=1/2\pi fC$. A plot of film-heating against conductance $1/R$ would therefore be as in figure 2, where the maximum heating occurs at the conductance $2\pi fC$. If conductance were proportional to thickness, that is conductivity independent of thickness, then the h.f. heating plotted against film-thickness would follow a similar curve. Actually, conductivity decreases as thickness decreases beyond some particular limit depending on the metal and conditions of deposition.

This causes the {heating, thickness} curve to differ in shape from figure 2, the nature of the modification indicating the dependence of conductivity on thickness and on the experimental conditions.

It is important to consider the effect of changes in conductance at constant thickness, such as might occur as a result of ageing at constant temperature or of temperature changes. To the left of the maximum in figure 2, a decrease in conductance which does not affect capacity will cause a decrease in heating, while to the right of the maximum a decrease in conductance will increase the heating. Changes in the film which vary the effective capacity will produce changes in the heating curve which will be more difficult to interpret. An insight into this effect was obtained experimentally by depositing on etched glass. In this case the film is broken up into regions each associated with an elementary capacity.

As regards the variation of resistance with temperature during a run when the h.f. field is applied, this will distort the {heating, thickness} curve in a manner which could be predicted if the dependence of resistivity on temperature were known for various thicknesses of film. This relation is, however, unknown for

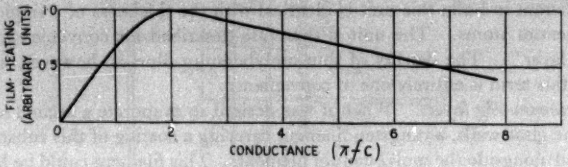

Figure 2.

the present films, though it was investigated by de Boer for his films[11]. Clearly this variation will not affect the determination of the thickness at which heating appears, nor will it affect the degree of heating occurring at maximum, so long as the heat treatment does not modify the geometrical form and dimensions of the elements of the film. These are the features of the curves which have been of greatest importance in their interpretation.

Assuming a resistivity of $5 \cdot 10^{-6}$ Ω./cm.[3], that of the bulk metal, it may be shown that at $3 \cdot 10^{7}$ c./sec. the skin effect will not be appreciable for films of thickness less than 10^{-5} cm. The resistivity will be greater than 5.10^{-6} in practice, so that any difference between h.f. and d.c. resistance will be due to structural conditions.

§4. RESULTS

In all cases, as film-thickness increases from zero, there is firstly a range over which no h.f. heating occurs, and secondly, a range where heating appears, increases to a maximum, and decreases again, as in figure 2. Results are shown in tabular form, giving the thickness at which heating appears, that at which heating is a maximum, and the thermocouple deflection at maximum heating. The experiments are in five series and are described in the five tables.

(4.1) *Treatment of glass.* (*a*) *Development of heating.* Table 1 shows that prolonged heat treatment of the glass before deposition commences is necessary to give the best conditions for formation of a film showing h.f. heating. Such treatment renders the glass surface more free from gas, and probably decreases roughness. The appearance of heating under these conditions at a thickness of 2·5 to 3 atomic layers is in agreement with the development of conductivity as observed under d.c. conditions by de Boer[5], and thus indicates similarity between h.f. and d.c. conductivities. The films on degassed glass are stable with time at all thicknesses, in contrast with those on glass which has been heat-treated for short periods only.

Table 1. Deposition on glass at room temperature

Duration and temperature of heating of glass in vacuo before commencement of deposition	Film-thickness (atomic layers) at incidence of heating	Film-thickness (atomic layers) at maximum heating	Maximum heating (thermo-couple deflection)	Effect of ageing at room temperature in vacuo
Lead glass				
(*a*) ½ hour at 400° c.	3·5	8·2	9·0	Thin films stable, thicker films show increase in h.f. heating.
(*b*) 5 hours at 400° c.	3·0	7·0	10·0	Thin films stable, thicker films show small increase in h.f. heating.
(*c*) 20 hours at 400° c.	2·5	6·5	11·0	Stable at all thicknesses.
(*d*) 60 hours at 400° c.	2·5	6·5	11·0	Stable at all thicknesses.
Hard glass				
(*e*) ½ hour at 520° c.	3·7	8·0	9·0	Similar to (*a*).
(*f*) 1 hour at 520° c.	2·6	6·8	11·0	Similar to (*b*).
(*g*) 5 hours at 520° c.	2·5	6·5	11·0	Similar to (*c*).
Lead glass etched 5 hours at 400° c.	5·0	9·2	7·0	Show increase in h.f. heating with time at all thicknesses.

The etching in case (*h*) was done with a hydrofluoric acid reagent and gave a surface with projections about $(10\,\mu.)^2$ in area and $10\,\mu.$ in height. The long delay before heating appears and the low maximum, in this case, are typical of the film in the broken-up state, and enable similar behaviour in other films to be interpreted as due to a similar state of the film.

Each result in table 1 was obtained as a mean from a number of experiments. Thus (*a*) was the mean of ten experiments in which the spread in the point at which heating appeared was from 3·0 to 4·6 layers, with a negligible spread in the slope of the {heating, thickness} curve before the maximum. The spread was less in cases (*b*) to (*d*), and greater in (*h*).

Some typical curves showing h.f. heating plotted against thickness are reproduced in figure 3. Curves (*a*), (*b*) and (*c*) show results (*a*), (*c*), (*h*), table 1, while (*d*) shows one of the results from table 2.

(*b*) *Visibility of film.* Observations of the thickness of film necessary to cause darkening of the glass were made. The filament support wire, figure 1, interrupts

the path of the atoms from filament to glass, and causes a shadow of clean glass to remain during film growth. Careful observation of this region of the bulbs enables a determination to be made of the thickness at which the film just becomes

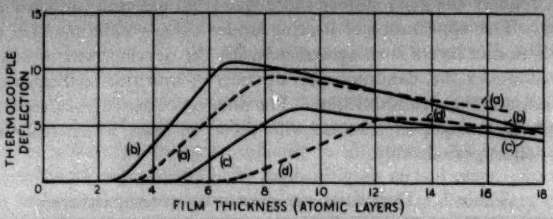

Figure 3. (*a*) Lead glass at room temperature. Incompletely degassed. (Baked ½ hour at 400° c.)
(*b*) Lead glass at room temperature. Thoroughly degassed. (Baked 20 hours at 400° c.)
(*c*) Lead glass at room temperature, etched, and hard glass at 340° c., not etched.
(*d*) Hard glass at 400° c.

visible. This thickness varies from 6 to 8 atomic layers in the case of deposition on clean degassed glass. General darkening as detected by viewing the bulb apart from the shadow region against a white background appears at from 12 to 15 layers. On etched glass, darkening appears at slightly greater thicknesses.

Table 2. Deposition on glass at different temperatures
Hard glass heated in vacuo at 520° c. before deposition commences
(*a*) for 1 hour, (*b*) for ½ hour

Temperature during deposition (°c.)	Film thickness (atomic layers) at incidence of heating	Film thickness (atomic layers) at maximum heating	Maximum heating (thermocouple deflection)	Effect of ageing at room temperature in vacuo
(*a*) 20	2·6	6·8	11·0	Stable at all thicknesses.
100	2·6	6·8	11·0	Stable at all thicknesses.
200	2·8	7·2	10·0	Stable at all thicknesses.
300	3·5	8·0	8·5	Unstable, showing increase in h.f. heating at all thicknesses.
350	4·8	9·2	7·0	Unstable, showing increase in h.f. heating at all thicknesses.
400	6·6	12·5	6·5	Unstable, showing increase in h.f. heating at all thicknesses.
450	8·0	16·0	6·0	Unstable, showing increase in h.f. heating at all thicknesses.
(*b*) 20	3·5	8·2	9·0	Thin films stable, thicker films show increase in h.f. heating.
100	3·5	8·4	9·0	Thin films stable, thicker films show increase in h.f. heating.
200	3·8	8·6	8·5	Thin films stable, thicker films show increase in h.f. heating.
300	6·0	10·2	7·0	Unstable, showing increase in h.f. heating at all thicknesses, more marked than in (*a*).
350	9·0	17·5	6·0	

It thus appears that considerable h.f. heating can occur in a film which is not visible, and that on clean glass the maximum heating occurs at 3.10^7 c./sec. in a film which is only detectable with difficulty.

(4.2) *Effect of temperature.* Table 2 shows the dependence of the results on the glass temperature during deposition in the case of hard glass. Deposition on lead glass gave similar results up to 300° c., but very erratic behaviour at higher temperatures. In case (*b*), the behaviour was erratic for hard glass also above 350°. These effects were traced to the molybdenum filament being attacked by water vapour produced by the glass at the higher temperatures, corresponding to the well-known reaction between tungsten and water vapour.

Comparison of (*a*) and (*b*), table 2, shows again the large effect due to incomplete degassing of the glass before deposition. This effect is now seen to increase with increasing temperature. The instability above 250° is also much more marked in case (*b*).

The effect of heating, in vacuo at 400° c., films deposited at various lower temperatures was investigated. Films deposited above 250° c. show at 400° c. an increase in h.f. heating at all thicknesses, similar to that occurring during room-temperature ageing, but proceeding more rapidly. Thus in 15 minutes at 400° c. the change is as great as in 16 hours at room temperature. Films deposited below 200° c. are much less affected by baking at 400° c.; prolonged baking does, however, modify the most stable films, producing an increase in heating in the thinner ones, and a decrease in the thicker ones. For example, the heating of a 4-atom film increased in 3 hours at 400° c. from 2 units to 4 units. This type of change corresponds to a decrease in resistance and is similar to the increase in d.c. conductivity observed by de Boer on baking a room-temperature film at 250° c.

(4.3) *Deposition on different substrates.* Table 3 shows the effect of depositing various substances on the glass after baking and before commencing molybdenum deposition. The oxides were formed by evaporation of films of the metals barium, aluminium and magnesium, followed by oxidation of the film and baking to remove excess oxygen. The fluorides were deposited by evaporation of coatings applied to the tungsten filament. In each case the fluoride film had a thickness of about 10^{-5} cm. The structure and properties of such films have been carefully investigated, and are described for example in reference (16). They consist of large numbers of crystals in the form of thin plates or lamellae, which are sufficiently separated to give a large internal surface, on which iodine and various metal atoms may be adsorbed. In the case of CaF_2, the lamellae have a thickness of about 2·5 mμ.; thus, on the average, the present film of CaF_2 is about 40 lamellae thick. Thus if molybdenum were adsorbed on the whole effective surface of the fluoride, 80 monatomic layers could be taken up in it.

It is well known that heat-treatment causes a sintering of the fluoride films, in which the crystals grow together. In some cases such a sintering occurs even at room temperature. It causes a decrease in the internal surface and in the amount of adsorption which can occur.

On depositing molybdenum in LiF or CaF_2, darkening of the glass due to the molybdenum became detectable at about 25 layers, as compared with about 6 layers on clean glass. The darkening then developed less rapidly than on clean glass. H.f. heating did not appear until about 40 layers. Thus the initial blackening must be ascribed to some dark-coloured but non-conducting surface compound. The slow development of the heating and the low maximum indicate clearly the lack of continuity in the films. Ageing occurred in all films at room temperature, as is indicated in table 3.

Table 3. Deposition on different substrates

Substrate	Film-thickness (atomic layers) for incidence of heating	Film-thickness (atomic layers) for maximum heating	Maximum heating (thermo-couple deflection)	Effect of ageing at room temperature in vacuo
BaO	9	32	7·0	All films unstable at all thicknesses, showing increase in h.f. heating with time.
Al_2O_3	15	43	6·5	
MgO	9	23	7·5	
LiF	35	52	7·5	
CaF_2	38	55	7·0	
Cryolite	26	40	8·0	
Phosphorus	6	12	9·0	

When the bulb was baked at 200° c., the changes in h.f. heating were similar to those during room-temperature ageing, but proceeded more rapidly. Thus in one hour the effect was as great as in sixteen hours at room temperature. Sintering also occurred during a bake at 200° in the films of LiF and CaF_2. This was indicated by the fact that subsequently deposition of molybdenum gave a {heating, thickness} curve similar to that obtained with clean glass. A bake at 400° produced similar effects in the thicker films, but in the thin ones caused an increase in resistance rather than the decrease associated with ageing. This may be due to the diffusion of molybdenum further into the fluoride.

(4.4) *Contamination with gases.* Molybdenum films were deposited on clean glass with a thickness such that the h.f. heating had not quite attained its maximum value. The effect of contact with oxygen and hydrogen was investigated and is indicated in table 4. In the stable type of film on degassed glass, contact with

Table 4. Effect of gases on films on clean glass

Treatment	Film-thickness (atomic layers)	Heating (thermocouple deflection) before contact with gas	Heating (thermocouple deflection) after contact with gas
Contact with O_2 at pressure of 50 μ. for $\frac{1}{2}$ hour	5	5	2
	7	9	4·5
Discharge in O_2 at 50 μ. for $\frac{1}{2}$ hour	7	9	0—1
Heating in O_2 at 50 μ. at 400° c. for $\frac{1}{2}$ hour	7	9	1—2
Contact with H_2 at 50 μ. for $\frac{1}{2}$ hour	7	9	9
Discharge in H_2 at 50 μ. for $\frac{1}{2}$ hour	7	9	9

oxygen causes a decrease in heating, and therefore an increase in resistance, corresponding to the oxidation of about two atomic layers of the film. Contact with

air at a pressure of 10 mm. or at atmospheric pressure has a similar effect, indicating that the degree of oxidation is almost independent of oxygen pressure.

A discharge in oxygen or baking in oxygen at 400° C. causes more complete oxidation than mere contact. A total thickness of about 15 layers may be oxidized completely by either means, though the effect is more rapid and more reliable in the discharge. Thicker films are partially oxidized.

Contact of oxygen or air with thicker films has a different type of effect. The thicker stable films of table 1 are not appreciably affected, but the unstable films of tables 1 and 2 respond very markedly. The changes during exposure to oxygen at room temperature are similar to those during ageing in vacuo, but much more rapid, indicating that the structural changes which occur during ageing are accelerated by oxidation. A similar acceleration occurs with films on oxides, but there is little effect with the films on fluorides. The ageing on oxidation of molybdenum has been described by de Boer[17], while a similar effect in other metals has been noted in work on their optical properties[9], [18]. Kindiger and Koller[18] consider that the taking up of gas without chemical change can decrease resistivity apart from structural changes.

If a thin film is exposed to oxygen and the oxygen is pumped away, there is no further change in heating as a result of heating in vacuo at 400° C., and when deposition is continued heating develops as with result (*a*), table 1. After exposure of the specimen to a discharge in oxygen, however, further oxidation occurs on heating in vacuo, and when deposition is continued there is a marked delay before h.f. heating begins to develop, as is indicated by (*b*), table 5. Thus in the presence of the discharge, oxidation occurs together with the adsorption of oxygen without reaction.

Table 5. Effect of electron bombardments

Type of film	Film-thickness (atomic layers)	Heating (thermcouple deflection) before bombardment	Heating (thermcouple deflection) after bombardment
(*a*) Film on clean lead glass pre-heated 5 hours at 400° C.	7	9	5
(*b*) Film on oxygen on glass	13	9	0
(*c*) Film on hydrogen on glass	4	2	7
	7	9	11
(*d*) Film on BaO	22	4·0	5·0
Film on LiF	36	1·0	7·0
	48	6·0	10·0
Film on CaF_2	39	1·0	5·5
Film on cryolite	30	1·0	3·0
Film on phosphorus	7	1·0	3·0

Neither contact with H_2 nor a discharge in H_2 has any effect on the h.f. heating, although in the latter case there is considerable clean-up of H_2 on the film. This probably takes place in the crystal boundaries.

(4.5) *Electron bombardment.* (*a*) *and* (*b*), *films containing oxygen.* Films of various types were bombarded with 300-volt electrons at a density of 1 ma. per cm^2 of film, causing a rise of temperature to 40° C. in half an hour. The results are shown

in table 5. For films on clean glass at room temperature, the effect is identical with that of exposure to oxygen. In films deposited on partially degassed glass, or on clean glass above 250° c., bombardment accelerates the ageing processes, the effect again resembling that of oxidation. It seems probable that the effect is, in fact, due to oxidation occurring on bombardment, since the film contains oxygen or an oxidizing agent, in spite of the fact that the glass is "thoroughly degassed".

This point was investigated by cleaning up oxygen on the glass surface, before deposition of the molybdenum, by passing a discharge through oxygen at a pressure of 50 μ. Result (*b*) shows the effect of bombarding a 13-atom film deposited on oxygen-covered glass; there is complete oxidation. Thicker films are partially oxidized. If the bulb is baked in oxygen before deposition of molybdenum commences, the same result is obtained. This result confirms the view expressed in the last paragraph; thus on glass baked for as much as five hours in vacuo at 400° c., there is considerable absorbed oxygen or oxidizing agent present and able to react with the metal of the film under appropriate conditions.

A similar conclusion was arrived at by Beeching[19] in the case of films of aluminium, chromium and copper. It remains uncertain, however, whether, under bombardment, oxidation is a necessary preliminary to the acceleration of ageing in the unstable films, or whether electrons could stimulate it in some degree in an oxygen-free film.

(*c*) *Films containing hydrogen.* After the glass had been baked, attempts were made to remove the last traces of oxygen from the glass and to replace it by hydrogen. Hydrogen was passed through the bulb at room temperature, the bulb was heated at 350°, in hydrogen, and, finally, a discharge through hydrogen cleaned up several atomic layers on the surface. Deposition of molybdenum then gave a curve resembling curve (*b*), figure 3. The result of bombarding a four-atom film is shown at (*c*), table 5.

This behaviour may be due to (1) an interaction between molybdenum and H_2; (2) a reduction of molybdenum oxide by H_2; or (3) a change in the film stimulated by electron bombardment when the glass is oxygen-free, the hydrogen playing no active part. If the last explanation is correct, the question at the end of the last section is answered. It should be noted that, in earlier work, no evidence was reported for changes in structure in films of other metals in the electron beam used in electron-diffraction experiments[9, 10]. Such evidence has, however, been obtained in more recent work[20].

(*d*) *Films deposited on oxides or fluorides* show an increase in h.f. heating at all thicknesses on electron bombardment, the effect being very marked with LiF and CaF_2. The effect is of the same type as that produced by ageing or heating in vacuo at 200° c., but more pronounced. Sintering does not occur, however, as it does during ageing or heating in vacuo, and this suggests that the effect is not due to rise of temperature. It was verified that the bombardment employed did not produce h.f. heating in the fluoride films tested before molybdenum deposition. More vigorous bombardment did produce the usual colouring effects which are frequently associated with the development of conductivity.

It was of interest to find out whether bombardment would produce h.f. heating in a film containing molybdenum but showing no heating initially. Bombardment of a 23-atom film which showed no darkening failed to give this result, but 2½ hours' bombardment of a 30-atom film which just showed darkening did produce a small h.f. heating which developed further in the following three hours. This indicates that, up to 25 atoms, the molybdenum is adsorbed on active centres, with van der Waals adsorption at greater thicknesses, since recrystallization under bombardment would be more probable when adsorption was of the second type.

It should be noted that bombardment of films showing a very small degree of heating leads to an increase in heating, as in the case of the hydrogen-contaminated films. It would be expected in such cases that oxidation would lead to a decrease in heating; only with a considerable thickness of conducting metal should oxidation lead to an ageing involving an increase in heating. Thus in these cases it appears that electron bombardment can stimulate a rearrangement in the film without an intermediate oxidation.

§ 5. VARIATION IN H.F. HEATING AT CONSTANT THICKNESS

Variations of this type have been found to occur as a consequence of ageing at room temperature, rise of temperature, contaminating with gases, or bombarding with electrons. Some of the variations may clearly be interpreted as resistance changes in the manner discussed in § 4.3.

The case in which h.f. heating increases at all thicknesses cannot be interpreted simply in this way. Such changes always occur in films showing a marked delay before the appearance of heating, and a low maximum. Such films, by analogy with those on etched glass showing the same effect, are initially discontinuous, and the increase in heating at all thicknesses indicates a development of greater continuity and uniformity in the film. This will be interpreted as due to an appropriate type of recrystallization. Such recrystallization has been observed in many types of film by means of electron-diffraction apparatus, and may consist in crystal growth or in reorientation of crystallites. It is probably associated with a relaxation of the strains set up during growth of the film, particularly when such growth takes place from isolated centres, as it will on a non-uniform or gas-contaminated surface. Strains and consequent recrystallization would be expected in films on etched glass or gas-contaminated glass, and on films of oxides or fluorides. The tendency to recrystallize in films deposited on glass above 250° c. is probably due to the fact that at high temperatures the first layer is discontinuous, agglomeration into small crystal aggregates occurring immediately after deposition. If that is so, the film grows in a state of strain from the isolated centres in this case also.

§ 6. REVIEW OF RESULTS

The development of h.f. heating with increasing thickness is most rapid with films deposited on clean degassed glass at temperatures below 200° c. It is slower above 250° c. when agglomeration occurs, or when the glass is etched, oxygen-contaminated, or covered with layers of oxides or fluorides. In the last

case internal adsorption of the metal leads to the possibility of very considerable deposition before h.f. heating appears. In each case of slow development of heating the film is discontinuous as on etched glass. It is also unstable, and can recrystallize even at room temperature, though more rapidly at higher temperatures. The films showing most rapid development of heating, though quite stable at room temperature, show a decrease in resistance during prolonged heating, for example at 400° c.

Thus in all cases in which a film is deposited in such a manner that the growth of h.f. heating with thickness is slow, the film is unstable, recrystallization in the direction of greater continuity occurring and leading to an increase in heating with time at all thicknesses. Thus in the practical case of a vacuum device running in a given h.f. field and having a given amount of metal deposited upon its walls, it is difficult by control of the conditions during deposition to obtain any permanent effect minimizing the losses in the film. Break-up of a low-temperature film at a higher temperature, causing an increase of resistance, does not occur, in contrast with many films which disintegrate on being heated when very thin. Oxidation is, however, a useful means of reducing the losses in a film provided it is sufficiently thin. With thicker films, oxidation may increase the losses, since recrystallization of the above type is accelerated by oxidation of the surface.

Electron bombardment causes oxidation of the film by oxidizing agents contained in it, and also causes recrystallization in the unstable films. In the case of films on clean glass, it is uncertain whether this recrystallization is entirely the result of oxidation or whether it might occur in the absence of oxygen. The point is difficult to decide, since in the present experiments it has not been possible to obtain complete freedom from oxygen, except possibly by saturating the surface with hydrogen, in which case it is uncertain what part the hydrogen may play. In films on oxides and fluorides it does appear, however, that bombardment may cause recrystallization without intermediate oxidation.

The outstanding results are the marked tendency of the molybdenum atoms to rearrange themselves, unless deposited on gas-free smooth glass below 250°, and the large part which can be played by gas present in the film and by surface irregularities. The importance of the presence of gas in the films has been realized in various ways. The present work in its early stages led the writer to suggest[21] that it was the presence of gas which led to the appearance of discontinuities in the {resistance, temperature} curves of films of various metals as studied by Kramer[6] and Fukuroi[22]. Later work by Fukuroi[23] showed this to be correct; evidently gas causes a delay in the onset of recrystallization as temperature rises, until it finally commences and proceeds almost to completion in a short temperature range, rather than gradually over a long one. Again, in work with very thoroughly degassed glass, Appleyard and Lovell[1]–[4] have found a positive temperature coefficient of resistance in their films. Most earlier workers, on the other hand, found a negative coefficient. De Boer[5] considers this a characteristic of the metal in the thin film, while other writers feel that it may be due to the presence of gas in the films.

The present work shows that films on glass baked for 5 hours at 400° C. are gas-contaminated; thus there would certainly be gas present in the molybdenum films examined by de Boer. It is interesting that deposition on glass known to be gas-contaminated * gave quite consistent results †, although the degree of contamination might be expected to vary considerably. This is important, in view of de Boer's point[24] concerning consistency of results.

In conclusion the author desires to tender his acknowledgements to the Marconi Co., Ltd., and The General Electric Co., Ltd., on whose behalf the work was carried out.

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* See (*a*), table 1.
† See § 4.1.

NOTE ON OPTICAL INSTRUMENTS OF SYMMETRICAL CONSTRUCTION

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ABSTRACT. The necessary and sufficient condition for freedom from aberrations at unit magnification in a holosymmetrical optical instrument is that parallel rays meeting the stop in diametrically opposite points shall intersect in the image surface. In hemisymmetrical systems each half must be corrected for all aberrations except distortion, the object being at infinity in the stop space.

OPTICAL instruments intended to produce an inverted image equal in size to the object are usually constructed so that one half of the system is a mirror image of the other half in a central transverse plane, which we will call the plane of the stop. It is well known that symmetry dispenses with any need to consider some at least of the unsymmetrical aberrations, such as coma and distortion, so that attention can be devoted entirely to the removal of symmetrical aberrations in one half of the instrument. It is not clear, though, exactly what conditions must be satisfied by the half system. For instance, if we cause the primary images of all points at infinity in the stop space to lie on the image surface, as we tend to do when ordinary ray-tracing methods are used, we may not satisfy all the conditions which should hold for skew rays. If, on the other hand, we bring the secondary images of these points at infinity on to the desired surface, we may introduce some needless limitations as well as fail to observe other conditions. We proceed to consider what conditions are necessary.

We suppose that (Y', Z') is a point of the object surface, which is a surface of revolution about the axis of the instrument, that (Y, Z) is the corresponding point of the image surface, and that a ray between the two intersects the symmetrical stop plane in (y, z). The corresponding direction cosines of the ray are (M', N'), (M, N) and (m, n) respectively. If the media are not of unit refractive index, these letters denote direction cosines multiplied by the refractive index.

These variables are connected by equations of odd order. For instance the variables of the image space are connected with those of the stop space by

$$\begin{pmatrix} M & -Y \\ N & -Z \end{pmatrix} = \begin{pmatrix} m & -y \\ n & -z \end{pmatrix} \begin{pmatrix} b & d \\ a & c \end{pmatrix} \qquad \ldots\ldots(1),$$

where a, b, c, d are functions of even order. The choice of variables is to some extent arbitrary—we will assume that the point coordinates are selected. Owing

to the rotational symmetry of the system there are only three variables in a, b, c, d, viz.: y^2+z^2, $yY+zZ$, and Y^2+Z^2. As is well known, a, b, c, d are not independent, but satisfy the identity $bc-ad=1$, so that the converse of (1) is

$$\begin{pmatrix} m & -y \\ n & -z \end{pmatrix} = \begin{pmatrix} M & -Y \\ N & -Z \end{pmatrix} \begin{pmatrix} c & -d \\ -a & b \end{pmatrix} \qquad \ldots\ldots(2).$$

Now if this system were reversed, so that light met the refracting surfaces in the opposite order, nothing in equations (1) and (2) would call for alteration except the direction cosines, which would simply have their signs reversed. If then a', b', c', d' are the functions for the first part of a holosymmetrical system corresponding to a, b, c, d respectively for the second part, corresponding to equation (2) we have

$$\begin{pmatrix} m & -y \\ n & -z \end{pmatrix} \begin{pmatrix} -1 & . \\ . & 1 \end{pmatrix} = \begin{pmatrix} M' & -Y' \\ N' & -Z' \end{pmatrix} \begin{pmatrix} -1 & . \\ . & 1 \end{pmatrix} \begin{pmatrix} c' & -d' \\ -a' & b' \end{pmatrix}$$

or, postmultiplying by $\begin{pmatrix} -1 & . \\ . & 1 \end{pmatrix}$,

$$\begin{pmatrix} m & -y \\ n & -z \end{pmatrix} = \begin{pmatrix} M' & -Y' \\ N' & -Z' \end{pmatrix} \begin{pmatrix} c' & d' \\ a' & b' \end{pmatrix} \qquad \ldots\ldots(3).$$

If we substitute from equation (3) in (1) we derive

$$\begin{pmatrix} M & -Y \\ N & -Z \end{pmatrix} = \begin{pmatrix} M' & -Y' \\ N' & -Z' \end{pmatrix} \begin{pmatrix} B & D \\ A & C \end{pmatrix} \qquad \ldots\ldots(4),$$

where

$$\left.\begin{aligned} A &= a'b+b'a, \\ B &= c'b+d'a, \\ C &= a'd+b'c, \\ D &= c'd+d'c. \end{aligned}\right\} \qquad \ldots\ldots(5).$$

Clearly from equation (4) the conditions for perfect imagery at unit magnification are $C\equiv-1$, $D\equiv0$. These suggest, from equations (5), $c=c'=0$; we should then also require $a'd=-1$, and since under these circumstances $ad=a'd'=-1$, this condition involves $a=a'$, $d=d'$. It is therefore insufficient to bring all the secondary foci for the half system on to the image surface. But although $c=c'=0$ are insufficient conditions, they are not necessary. For if we substitute from equation (4) in equation (2), putting $B=C=-1$ and $D=0$, and compare with equation (3), we have

$$\begin{pmatrix} c' & d' \\ a' & b' \end{pmatrix} = \begin{pmatrix} -1 & . \\ A & -1 \end{pmatrix} \begin{pmatrix} c & -d \\ -a & b \end{pmatrix} = \begin{pmatrix} -c & d \\ Ac+a & -Ad-b \end{pmatrix};$$

i.e.

$$\left.\begin{aligned} c &= -c' \\ d &= d' \end{aligned}\right\} \qquad \ldots\ldots(6)$$

are necessary conditions. It is seen immediately from equations (5) that they are sufficient.

Now c' and d' are the same functions of y^2+z^2, $yY'+zZ'$, $Y'^2+Z'^2$ that c and d

are of y^2+z^2, $yY+zZ$, Y^2+Z^2. These two sets of variables only differ from one another in the signs of their middle members. It follows that the conditions (6) merely require c to be an odd and d an even function of $yY+zZ$, or, from equation (1), Y and Z to be even functions of y and z.

We can express this condition very simply in terms of rays. Let us define a diametral pair of rays * as any two rays parallel to one another in the stop space which intersect the stop plane in diametrically opposite points, so that the mid-point of the line joining these intersections is the axial point of the plane. Then the condition to be satisfied by the half system is that every diametral pair of rays meets after refraction in the image surface. This follows at once from equation (1), by regarding the expressions for Y and Z as equations for m and n. This condition is readily seen to be both necessary and sufficient.

It may be of interest to add a formal verification of this conclusion using the characteristic function. If V represents the length of the optical path from (y, z) to (Y, Z) as a function of y, z, Y, Z, the condition that m, i.e. $-\partial V/\partial y$, should be an even function of y and z of the form required by equation (1) shows that the general form to assume for V is

$$V=f(Y^2+Z^2)+(yY+zZ)F[y^2+z^2,\ Y^2+Z^2,\ (yY+zZ)^2].$$

The corresponding function V' for the first part of the system is

$$V'=f(Y'^2+Z'^2)+(yY'+zZ')F[y^2+z^2,\ Y'^2+Z'^2,\ (yY'+zZ')^2].$$

The conditions

$$\frac{\partial}{\partial y}(V+V')=\frac{\partial}{\partial z}(V+V')=0$$

give

$$Y+Y'=Z+Z'=0,$$

and it then follows that

$$V+V'=2f(Y^2+Z^2),$$

so that the optical path through a given image point is the same for all rays.

The simplicity of the condition to be satisfied by the half system is due to the equality in dimensions of the two parts. If we combine two systems which satisfy this condition but are unequal, there is no assurance that Y and Z will not vary with y and z as well as with Y' and Z'. To obtain unique relations between the pairs Y, Y' and Z, Z', parallel rays through all points of a diameter of the stop must meet the image surface in a common point, and, since all diameters pass through the centre, this implies that all parallel rays in the stop space must be refracted to the same image point. That is to say, in a hemisymmetrical instrument each half must be completely corrected for all aberrations except distortion, the object being at infinity.

* It should be noted that this is entirely different from Conrady's *D* pair, which merely determines a secondary focus.

REVIEWS OF BOOKS

Introduction to Contemporary Physics, by Karl K. Darrow. 2nd edition. Pp. xi +648. (London : Macmillan and Co., 1939.) 25*s*. net.

In 1926, when wave mechanics was barely a year old, seven years after Rutherford had first realized that alpha particles could break up the nuclei of some of the lighter elements, and six years before the first artificially accelerated ions had been used by Cockcroft and Walton to effect transmutations, Darrow published the first edition of his *Contemporary Physics*. That edition contributed much to the spread of knowledge of what was then contemporary physics, and the new edition shows that its author is still one of the most gifted expositors we have. He has not merely polished the book up and fitted in the new work; he has recast it entirely (the number of misprints, even in the early pages, would alone be evidence of this), aiming at a logical rather than a historical order of development.

In the first part, the extranuclear constitution of the atom is considered. We first meet the electron as a particle detached from atoms, and then study the nuclear model of the atom and, in particular, its electron shells. The energy states are introduced through critical-potential measurements, rather than through the spectroscopic evidence, but before this comes the evidence for the wave aspect of the electron and other particles.

The second part of the book deals with the nucleus, as revealed by transmutation experiments, and with neutrons. In conformity with the plan adopted, the problems of naturally radio-active elements are left till the end. They are now seen to fall into the scheme built up on experimental evidence, instead of, as in the historical development, providing the clues which led to a tentative scheme and in turn stimulated the experimental attack.

The book is no popular exposition for the layman. Mathematics, of a simple kind, is not shirked, and the author has not spared himself in collecting the most recent data, even where accurate values are not essential to the argument. Here and there he offers definitely original suggestions. There can be few physicists who would not enjoy reading this book, and few who would not feel the time so spent had been used profitably.

J. H. A.

Introduction to Mechanics and Heat, by Nathaniel H. Frank. 2nd edition. Pp. xvi+384. (London: McGraw-Hill, 1939.) 18*s*.

The author of this book is a professor of physics at the Massachusetts Institute of Technology, and the ground covered is that of the first year of a two years' course of physics. The volume under review is the second edition, and embodies a number of improvements suggested by four years of use of the first edition in class teaching. The author has endeavoured to develop a logical treatment of mechanics, acoustics and heat so that the student may be equipped to utilize fundamental and general methods of attack on problems in various branches of physics. After some definitions a start is made on linear kinematics of a mass point, and this subject is so treated as to lessen the difficulties that confront the student who is learning the elements of the calculus at the same time. Again, in the chapter on plane kinematics of a mass point there is a geometrical proof

of radial acceleration in circular motion which brings out clearly the concept of the rate of change of a rotating vector.

The discussion of planetary motion and of gravitation is placed after the chapters on the statics and dynamics of a rigid body so as to serve as introduction to the general concept of force fields. Thus a smooth transition is made to the mechanics of continuous media. The latter subject is treated more extensively than in most elementary discussions so as to impress on the student that the general principles employed in particle and rigid body mechanics are identical. Descriptive material has been cut down to a minimum, as the author believes that much descriptive physics interspersed with a logical systematic development of physical principles tends to hinder the student from grasping the well-ordered continuity of thought and method pervading the whole quantitative structure of physics.

A valuable feature of the book is the group of problems included at the end of each chapter, though the curiosity of the reviewer was aroused by the wording of one of the examples: "A popfly is caught by the catcher 6 seconds after being struck. How high did it rise?"

The volume is one which can be warmly recommended to the consideration of teachers of physics in this country. E. G.

Physics of the Earth.—VII : *Internal Constitution of the Earth.* Edited by B. Gutenberg. Pp. x+413. (London: McGraw-Hill, 1939.) 30*s*.

This is a co-operative work designed by the U.S. National Research Council, and originally planned in 1926. On account of various delays Dr Gutenberg was placed in charge in 1937, and has now succeeded in getting it revised and issued. He remarks in the preface that differences of opinion between various contributors, which are perhaps inevitable in a rapidly growing subject, have been deliberately made prominent; this should attract attention to the places where further work will do most good.

The reviewer's opinion of Chapter I, by Dr Harold Jeffreys on the origin of the solar system, must be kept private. Professor R. A. Daly deals with relevant facts and inferences from field geology, and has managed to condense an enormous amount of information into a small space. It is necessary, however, to question his acceptance of the view that the uplift that is proceeding in Scandinavia is due to a viscous readjustment of isostatic type, following the removal of the load of ice at the end of the last glacial period; this applies equally to numerous allusions by Gutenberg in later chapters. There is no mention of the fact that even where isostasy fits the gravity observations best, the average residual after allowance for it is about six times the observational error, and as large as in Scandinavia. In most regions there is no evidence of change of level. In Cyprus the recent work of Mace shows large positive anomalies. Here there has been no change of level in historic times, but there have been uplifts since the Pleistocene: the land rose in spite of the region being too heavy. Changes of level in the Great Lakes region have been claimed as supporting the argument from Scandinavia; but one would expect the change to have been greater on the shore of Hudson Bay, where the ice would have been thicker. Here the work of J. B. Tyrrell and W. A. Johnston shows no sign of uplift. The argument from Scandinavia is, in fact, the selection of the one case that is consistent with a particular hypothesis, while all evidence against it is ignored. There is evidence for isostasy as a rough approximation in many regions; there is evidence also for changes of level; but the two facts are not related in any way consistent with the

idea that there is an underlying layer of uniform viscosity that yields passively to a surface load. They are consistent with the view that the underlying layer is strong and is undergoing changes of form of its own accord, to which the upper layers have to adjust themselves.

Dr L. H. Adams discusses the laboratory data about the elastic properties of rocks. Besides the work at the Geophysical Laboratory, to which he has contributed so much, that at Harvard is treated. The apparent discrepancies between the compressibility measures have now been cleared up. The results are compared with seismological data. The reviewer would have liked to see something about his own method of comparison, in terms of k/ρ (bulk-modulus divided by density), which can be estimated both from laboratory evidence and from seismology; it is rather more direct, is free from possible complications due to imperfection of elasticity, and makes no hypothesis about Poisson's ratio. The Harvard results yield laboratory estimates of the latter, but these do not appear consistent with any possible identifications of the materials. Is there still some systematic error in the measures of rigidity?

The composition of the crust and the relation of the crust to the interior are treated by the late H. S. Washington; his article has been revised by Dr Adams. The details about meteorites are valuable.

Dr C. E. van Orstrand contributes a list of measures of the vertical gradient of temperature in the crust. Unfortunately they are not accompanied by measures of the thermal conductivities of the rocks in the same places, so that they do not yield estimates of the outward flow of heat. We badly need to know how far the variation of the temperature-gradient represents differences of heat flow from place to place, and how far it is merely a result of variation of conductivity near the surface. Work on this is proceeding in this country, but needs to be extended to other regions.

Gutenberg treats the cooling of the earth. He mentions two arguments due to McNish and Bridgman, suggesting that the thermal conductivity may increase with depth, especially at the depth where there is an indication of a large increase of electrical conductivity. This will need attention, but at the moment is not the most important uncertainty in the problem. A reference is made to the possibility of substances with a maximum melting-point under increase of pressure, but not to Bridgman's failure to find such substances whose melting points lay within the range accessible to experiment. It at least showed that F. Wolff's quadratic extrapolation does not fit any known case. Dr Gutenberg remarks that "it is conceivable that more heat is generated by radioactive matter inside the earth than escapes through the surface" (p. 166). The opinion in question is not his own, but he does not give the most effective argument against it. Storage of heat would lead to fusion, which contradicts the existence of distortional waves; and even if the properties were such that convection currents could arise before fusion, they would transfer the heat upwards as fast as it was generated, and the effect would be an increase in the temperature gradient at the surface till it was great enough for the whole of the heat to be carried off. The belief is traceable to the naïve notion of certain geochemists that rocks are definite chemical compounds, the radioactive constituents constituting the same fraction of any rock with similar major constituents, irrespective of its history and of the depth where it occurs. When the distribution with depth is treated as one of the unknowns of the problem there is no difficulty.

Gutenberg, accepting a finite viscosity for the interior of the earth, bases an explanation of geological processes on convection currents. The trouble here is that with a steady supply of heat there is no provision for a variation of the stress with time. Either the drag on the base of the strong layers is enough to fracture them or it is not; in one case

it would give mountain-formation all the time, in the other not at all. There is no provision for the fact that mountain-formation has occurred over short stretches of geological time, separated by long intervals of quiescence. In material with a finite strength undergoing secular contraction the situation is entirely different. Here the stresses build up till fracture occurs; this releases most of them, and they proceed to build up again; the intermittence is explained. It apparently cannot be explained on any hypothesis involving a finite viscosity; and such a hypothesis would also imply perfect isostasy, which is contrary to the facts.

It should be said that all the authors who mention Wegener reject his reconstruction; but Gutenberg appeals to convection currents or a tendency of continents to flow apart to explain how all the present continents could have separated from a single primitive one. The force between two floating continents, however, is an attraction, and in any case is much less than the Eötvös equatorward one. It may be remarked that Wegener's opinion that the latter would give a westerly drift rested on a mistake in dynamics; the alleged drift of Greenland, even if it were verified, would not support the hypothesis that it is producing any movement, while the failure to find continuous changes of latitude is strong evidence against both it and any shift of the pole.

Gutenberg remarks (p. 206): "In all theories of mountain formation, relatively large horizontal and vertical movements must be assumed. It is only a short step to the conclusion that the distances between the continents have changed." The former are of the order of 50 to 300 km., according to the number of stages of mountain-formation covered. The latter are of the order of 5000 to 10,000 km. Some short step!

Prof. J. B. Macelwane summarizes the evidence about the velocities of seismic waves. In some places he disagrees with Gutenberg; in these I agree with Gutenberg. One special point is in the treatment of group velocity in surface waves (p. 240). The theory of dispersion leads to a group velocity associated with each period, provided that this is not too near the largest or the smallest group velocity possible. It is therefore in any case invalid to consider waves near the beginning of the train and to apply the theory to them. Further, the waves of a given period arriving at different distances are not identical according to the theory. An individual wave should theoretically increase in period as it advances. The increase in the length of the train as it advances is produced by the continual appearance of new waves at its rear. The group velocity arises simply in an approximation of a well-known type (the method of steepest descents) when applied to the integrals that give the displacement at a distance generated by a sudden disturbance at the origin. There is no such thing as the "hypothesis of group velocity."

Gutenberg gives useful information, based on recent papers by himself and Richter, about deep-focus earthquakes. But he seems to think that it is sufficient for the generation of large deep earthquakes that large *strains* should be produced; large *stresses* are necessary, and these would be dissipated rapidly in a region of low strength.

Dr W. D. Lambert gives a brief but good account of the figure of the earth and the corresponding density distribution. Gutenberg proceeds to the distribution of the elastic constants, including data from seismology, the 14-monthly variation of latitude, and the bodily tide. He then discusses types of imperfection of elasticity. He seems to have misread a word in a letter from me, and in consequence makes far too much of a type that I discussed in *The Earth* and called "firmo-viscosity." (Some other writers have used the same form under the name "visco-elasticity," which must be carefully distinguished from elastico-viscosity.) This form leads to hopelessly incorrect results for vibrations of short period, and if a simple linear form is to be used to illustrate elastic afterworking it should be the one that Gutenberg mentions only in passing on p. 363.

The book contains an enormous amount of valuable information; the authors have read widely, and the references make it a necessary source-book. But just for that reason it is important that the mistakes, especially the reiterated ones, should be pointed out as soon as possible. HAROLD JEFFREYS.

The Mathematical Theory of Non-uniform Gases, by S. Chapman and T. G. Cowling. Pp. xxiii+404. (Cambridge University Press, 1939.) 30*s*. net.

Among the large number of books published every year on all branches of physics those on kinetic theory are few and far between; this is a tribute to the quality of the standard text-books, but it is nevertheless desirable to have from time to time fresh viewpoints as well as accounts of the latest work. This new book by Professor Chapman and Dr Cowling gives, as is to be expected, an authoritative account of the mathematical theory.

The scope of the book has been limited to those aspects of kinetic theory which are concerned with the solution of the Maxwell-Boltzmann equation, i.e. transport phenomena. The modifications introduced by quantum theory also are considered, and the mathematical treatment has been carried through in a very complete manner. The initial chapters (1 to 6) deal with the simpler aspects of kinetic theory leading up to the Maxwell-Boltzmann equation. Special chapters (7 to 9) are devoted to the solution of this equation and to the calculation of general expressions for the viscosity, thermal conductivity, and diffusion in simple gases and in gas mixtures. These general expressions are then evaluated (chapter 10) for different types of interaction between the particles of the gas and in the special case where one of the constituents in a mixture has a small mass—which is of importance in the discussion of the behaviour of electrons in gases. After an extension of the theory to rough spherical molecules, a comparison is made of the results of the theoretical investigations with the experimental data on viscosity, thermal conductivity and diffusion (chapters 12, 13, 14). The theoretical formulae have been summarized here with the object of rendering these chapters accessible to experimental physicists and chemists. The results of the theory depend on the law of force between the particles in the gas, and these laws are subjected to a careful examination. It is shown that fields consisting of both attractive and repulsive forces contain too many parameters to allow these to be uniquely determined, and the comparison with experiment is made finally with repulsive forces only. Two further chapters, on higher-order solutions of the Maxwell-Boltzmann equation (15) and on dense gases (16), conclude the classical theory. The modifications necessitated by quantum theory are then considered (chapter 17). A brief sketch of the quantum theory of elastic collisions and of quantum statistics leads up to the discussion of transport phenomena for degenerate gases. In the final chapter (18) the general theory is applied to the behaviour of ionized gases under the action of electrostatic, magnetic, and electromagnetic fields.

The book has been produced extremely well, the very clear presentation of complicated formulae being a noteworthy feature. The proofs seem to have been read very carefully and the references are fully adequate. On page 295 the formula given for the wave-length associated with two interacting particles differs from the de Broglie formula by 2π—a point likely to cause confusion. A statement which should be revised in a future edition occurs on page 300, viz.: "Experiments have not been carried out with uncharged particles, but measurements of free paths for electrons and positive ions have been made." An appreciable amount of experimental work on molecular rays has, in

fact, been devoted to the measurement of the scattering of uncharged particles in gases. A discussion of the atomic and molecular diameters found in this way would be of some interest. This is, however, a small point in an essentially mathematical presentation, and one can have no hesitation in saying that the book will be of great value both to the advanced student and to the research worker. M. B.

Atombau und Spektrallinien, Vol. 2, by Arnold Sommerfeld. 2nd edition. Pp. xi+819. (Braunschweig: Vieweg, 1939.) RM. 35, bound RM. 38.

This second volume of Professor Sommerfeld's *Atombau und Spektrallinien* is a new edition of the well-known *Wellenmechanischer Ergänzungsband*. The general scope of the book remains the same as in the first edition, but many parts have been greatly extended and additional matter has been introduced.

The chapters on the Schrödinger theory, on its applications to special problems, on perturbation theory, and on operator theory are practically unaltered; the Dirac theory of the electron (which had just been published at the time of the first edition) is now dealt with very fully, and special chapters are devoted to the photoelectric effect, the Compton effect, and the continuous x-ray spectrum. A completely new chapter contains an account of approximate methods of calculating eigenfunctions; in this is also a section on the theory of the Thomas-Fermi atom.

Because of the limitation of the scope of the book it has been possible to give detailed discussions of many points usually only touched upon in text-books on wave mechanics. It is hardly necessary to add that it will be welcomed by all theoretical physicists. M. B.

Hand- und Jahrbuch der Chemischen Physik, Vol. 3, Part 2, Sections III-IV. Pp. 276. (Leipzig: Akademische Verlagsgesellschaft M.B.H., 1939.) RM. 28.20.

Section III of this volume of the *Handbook* consists of an article by Professor A. Sommerfeld and Dr. L. Waldmann which gives a clear exposition of classical statistics, quantum statistics, their relation to one another and to thermodynamics. The discussion is confined mainly to the ideal gases, monatomic and polyatomic, but a special section is included on van der Waals gases and on the problem of condensation. Section IV contains a full account, by Professor K. F. Herzfeld, of the theoretical and experimental aspects of the kinetic theory of gases; special parts are devoted to the scattering of atoms, ions and electrons, and to the interaction of gases with solid surfaces. M. B.

Hand- und Jahrbuch der Chemischen Physik, Vol. 10, Part III. Pp. 104. (Leipzig: Akademische Verlagsgesellschaft M.B.H., 1939.) RM. 12.

This part of the *Handbook* consists of two articles. The first, by Dr. B. Mrowka, gives a concise account of the results of the theoretical and experimental investigations of the Stark effect in hydrogen, helium and more complicated atoms. The second—an article on the Kerr effect by Dr. H. A. Stuart—forms an admirable review of the theoretical and experimental work (much of the latter his own) in this field. A great deal of experimental material has been collected in the form of tables; those on gases are used in a detailed comparison with the predictions of the Born-Langevin theory, those on liquids will be of value in testing future theories. A very interesting account is also given of the use to which data on polarizibility (derived from the Kerr effect and from other sources) can be put in the determination of molecular structure. M. B.

Matter and Light: The New Physics, by Louis de Broglie. Translated by W. H. Johnston. Pp. 300. (London: Macmillan and Co. Ltd., 1939.) 12*s*. 6*d*. net.

This book is a collection of delightful essays on the development and attainments of quantum mechanics since the introduction of the new ideas of which the author is the pioneer. The book is divided into seven sections containing a group of chapters, each of which is of the nature of an essay. The first four sections are upon purely physical subjects. They deal with parts of the history of physics especially revealing gaps and weaknesses which suggest the need for closer examination and the need for readjustment of deep-seated ideas. They also give an account of the way in which the recent developments propose a solution of the problems suggested.

An interesting study under the title "The undulatory aspects of the electron" is of especial interest, since it was delivered as a lecture on the occasion of the receipt of the Nobel Prize Award. It throws light on the processes of thought by which the association of corpuscule and wave developed as a guiding principle in the new advance.

French writers on physical subjects have earned a reputation for clarity and care in exposition amongst their English colleagues, and Professor de Broglie has contributed to the establishment of this reputation in no small degree. In this book, which is non-mathematical in character, the reader will find another example of clear and cogent argument. The essays are written independently of one another, and, consequently, there is some repetition throughout, but this plan has the advantage that the reader may open the book anywhere and find no need to refer to previous pages.

Perhaps too much has been made of the uncertainty relations which the author describes as a principle. But these important conditions do not merit the title of a principle; they are the result of the adoption of the principle of basing an explanation of certain phenomena on the analogy with optics, which might be described as "Schroedinger's principle," since it was he who, guided and stimulated by the author's ideas, first put it into exact expression.

Once the wave conception is accepted, the uncertainty relations follow. Indeed, they are not new in optics but, taken with de Broglie's ideas, they throw light on the limitation which bounds our mode of description in corpuscular physics. The new quantum theory has taught us perhaps as much about the nature of our method of description in physics as about the details of physics itself.

In this connection a remark in the preface is interesting. The author writes of the somewhat ingenuous realism of earlier thinkers, but then goes on to ask who knows what mysteries are hidden within the nucleus of the atom. It would be a pity to banish ingenuousness from scientific research, and surely this remark shows that it still exists in even the foremost among the workers upon the quantum theory. There are some who would answer, and without cynicism, that we shall discover just what we are prepared to place there. We are back at the question whether the atom was discovered or made.

This book brings out clearly the importance of a right notation for describing the story of the physical world, and also shows, especially in the section on light and radiation, that it has not yet been found. Physics remains the same, space and time continue, ingenuousness is still with us, but the story is told again and again and it is always better and gains in the repetition.

The last two sections are described as philosophical studies, and they are interesting as expressing the author's thoughts on a subject which has received a new stimulus from the change of outlook in physics. The introduction of the uncertainty relations has naturally turned attention to the fascinating subject of determinism both within and

outside physics, but it is well to call to mind a remark made by an authority on the subject of relativity. He wrote: "Relativity is physics and has nothing to do with philosophy", and we may apply this also to the quantum theory. Philosophers can gain stimulus from the new ideas of physicists, but the latter, remembering their mistakes on the subject of determinism, can avoid making similar mistakes on the subject of indeterminism.

H. T. F.

Tables for Converting Rectangular to Polar Co-ordinates, by J. C. P. Miller. 16 pp. (London: Scientific Computing Service, Ltd., 1939.) 2*s*.

The utility of these tables must depend on the frequency with which the user has need of transforming from rectangular co-ordinates (x, y) to polar co-ordinates (r, θ). If he carries out the operation relatively rarely, he will use some such scheme as one of the following: (*a*) subtract $\log|x|$ from $\log|y|$, so obtaining $\log\tan\theta$, whence θ is obtained direct from tables. Then subtract $\log\cos\theta$ from $\log x$ (which is already known), obtain a check by subtracting $\log\sin\theta$ from $\log y$, the common value being that of $\log r$. (*b*) with slide-rule alone, θ or its complement may be read off on the scale at the back of the slide, if on the front the rule is set to give y/x or its reciprocal. Then r may be obtained from $\sin\theta$ on the back and y on the front, the check being obtained by calculating r directly as $y[1+(x/y)^2]^{\frac{1}{2}}$ with the slide-rule.

With these methods, the quadrant in which the angle occurs, and the modifications necessary when it is more accurate to calculate the complement of θ rather than the angle itself, require thinking out on each occasion. The frequent user of these tables is spared this need, since both the angle and its complement are tabulated, and a semi-pictorial scheme at the foot of each page shows the choice to be made; to the uninitiated, however, the use of the scheme requires as much mental effort as the direct deduction would involve. The method adopted is to compute k=the smaller of y/x or x/y (by means of a slide-rule or otherwise), and then the table gives θ and $\sqrt{(1+k^2)}$. From this r is obtained by use of the slide-rule again since $r=y\sqrt{(1+k^2)}$ or $x\sqrt{(1+k^2)}$. The angle θ and its complement are tabulated in degrees, and θ itself in radians, as functions of k, which runs from 0 to 1 by intervals of 0·001.

J. H. A.

Explosions- und Verbrennungs-vorgänge in Gasen, by Wilhelm Jost. Pp. viii+608, with 277 diagrams. (Berlin: Springer, 1939.) RM. 46.50, bound RM. 49.50.

This book is a comprehensive summary of our present-day knowledge of gaseous-explosion and flame phenomena, dealing with the theoretical and experimental results obtained up to April 1939. This work has been subdivided into thirteen chapters, the headings of which indicate the scope of the book. They are: the thermodynamics of explosion processes, spontaneous and induced ignition, propagation of explosions in open and closed vessels, detonation, flames, kinetics of combustion and explosion reactions, the hydrogen-oxygen and carbon monoxide-oxygen reactions, reactions in the electric discharge, the combustion of hydrocarbons and the chemical processes occurring in the internal-combustion and Diesel engines.

The author's style is clear, and in presenting details of work which has not yet been satisfactorily interpreted he has maintained an admirable balance. Indeed, the only criticism that the reviewer has to make is the inclusion of short sections which summarize the foundations of the kinetic theory of gases and the theory of gaseous reactions respectively. These are surely out of place in a book of this standing.

Of the production and illustration of the book it is necessary only to say that they fully maintain the high standard set by the publishers in their previous scientific monographs. It is to be deplored that the very high price, and the, presumably small, number of copies available in England will combine to place it beyond the reach of the many workers who would otherwise profit by its publication. R. F. B.

Ferromagnetismus, by R. Becker and W. Döring. Pp. vii+440. (Berlin: Julius Springer, 1939.) RM. 39.

In recent years there have been considerable developments in our knowledge of ferromagnetism, more especially in the application of the domain theory to technical magnetization processes, and although there is still much to be done before the theory is complete, the time was certainly ripe for a survey of the present state of our knowledge. In this book Professor Becker and Dr Döring have given a treatise on those aspects of magnetization, magnetostriction, magnetization under strain and allied phenomena of which they and their co-workers at Göttingen have been among the leading exponents. Although the book is an amplification of a series of lectures given to an audience of technical magneticians in Berlin in the winter of 1934–5, its value to the latter is somewhat diminished by the inclusion of a considerable quantity of rather heavy mathematics. There is little doubt that some, at any rate, of this could have been omitted without impairing the continuity of the work, but its inclusion will be welcomed by workers on theoretical magnetism, as it eliminates some of the unnecessary consultation of original papers which is the inevitable consequence of the more usual fault of omitting essential sections of the treatment.

The book may be conveniently considered in three parts. The first two chapters are almost entirely of a theoretical nature; chapter 1 deals with magnetism in general and has sections on para- and diamagnetism, while chapter 2 deals with the theories relevant to ferromagnetism, and these are discussed in conjunction with the experimental results, later in the book. The next three chapters may best be described as covering the domain theory of technical magnetization, and they include much work which had not hitherto been published on both the practical and theoretical aspects. There are sections on internal energy, energy of domain walls, initial permeability and coercive force, the ΔE effect, magnetostriction, damping of mechnical vibrations—in fact, any topic which is included under the main heading will be found somewhere in this section. The final chapter is concerned with ferromagnetic materials and their applications, and such matters as the problem of permalloy, annealing in a magnetic field and anistropic plates of alloys are also considered.

It is unfortunate that the War should have intervened before this work could have become well known in this country, but it is to be hoped that when happier times return, it will be accorded the careful attention which its thorough and detailed treatment truly merits. J. C. W.

Introductory Quantum Mechanics, by V. Rojansky. Pp. x+544. (London and Glasgow: Blackie and Son, Ltd., 1939.) 22*s.* 6*d.* net.

Here is a book on quantum mechanics for those physicists and chemists who want more than a popular or semi-popular account, but for whom the mathematical difficulties of advanced treatises and original papers may prove a stumbling block. The author takes it for granted that the reader has some knowledge of the main ideas and results

of quantum theory and proceeds at once to their mathematical formulation. The first chapter is devoted to the vital notions of differential operators, their eigen values and eigen functions; the second, to showing that in certain circumstances the solutions of problems in classical mechanics must be expressed in terms of probability-distribution functions which are of the essence of quantum mechanics. The subject proper is introduced through two basic postulates associating dynamical variables with operators. From these postulates as starting-point the author develops in turn the wave mechanics of Schrödinger, the corresponding momentum method, Heisenberg's matrix mechanics and the symbolic method of Dirac. In each case the treatment is confined to the one-dimensional motion of a particle. Three-dimensional motion is first considered in the twelfth chapter, which contains the Schrödinger wave theory of the hydrogen atom. The final two chapters deal respectively with Pauli's theory of electron spin and Dirac's relativistic wave equation of the electron.

The author writes in an easy, intimate style, and is obviously at pains to anticipate and explain in detail every possible point of difficulty. The conscientious reader who works through this book without omitting the many illuminating exercises can hardly fail to acquire a sound knowledge of the theory and its implications and at the same time a certain mastery of the mathematical methods. In this sense the book is in the tradition of Jeans' *Electricity and Magnetism*.

Some regret may be felt at the exclusion of even brief accounts of crucial experiments, such as those of Stern and Gerlach or of Davisson and Germer, showing how the theoretical results are borne out in practice. It is also a pity that motion in an electromagnetic field has had to be omitted.

The author may be congratulated on producing one of the first genuine text-books of quantum mechanics and one which reaches a high standard. W. S. S.

Modern Machine Calculation. Pp. 74, with one plate inset. (London: Scientific Computing Services, Ltd., 1939.) 5*s*.

This booklet is largely a translation by Dr L. J. Comrie and Dr H. O. Hartley of the manual written by Mr H. Sabielny on the use of the Model LX Facit Calculating Machine. The capacity of this machine is 10 figures in both the setting and multiplier registers, and 19 figures in the product. The product and multiplier registers are contained in a moving carriage; the setting register, which is entered by ten keys, is fixed. An important addition is the division tabulator, for moving the number set in this register to the extreme left position. The machine is hand operated, works in either direction, and has tens transmission throughout. Clearing is by separate levers. The usual locking arrangements to prevent misuse of the mechanism are provided, and there are no fancy features.

The manual is written to give all the guidance needed by anyone with no previous experience of calculating machines—almost, indeed, with no more than the most elementary knowledge of arithmetic. The text is well illustrated with examples, mostly applications of the machine to commercial calculations. The learner will be wise if he follows the instructions carefully, for they include advice on what he should do with his eyes, on short cutting, on rounding off, on the considerations that should determine which of three methods of division should be adopted (a fourth is mentioned which should never be used), and the value to the operator of certain tables. Then there are explained ingenious ways of reducing calculations that normally necessitate two successive operations to only one. These are probably not all known even to many computers of long experience. The translators have added a section on calculations involving sterling and British

weights and measures with a decimal machine, and have added 13 useful tables. They have also made a number of additions to the original text which their experience has suggested, including what they believe to be a new method of doing rule-of-three calculations in one operation without setting complements or using complementary division.

Although it will be realized that the manual has not been written for scientific workers, the translators state that the machine is eminently suited to general scientific calculations.

T. S.

Text Book of Quantitative Inorganic Analysis, by A. I. Vogel. Pp. xix+856. (London: Longmans, Green and Co., 1939.) 18*s*.

In preparing a text-book on the theory and practice of quantitative analysis, designed to cover the needs of students throughout their chemical training, and, at the same time, to appeal to practising analytical chemists, the author has undertaken a very ambitious task, and it is not therefore too harsh a criticism to suggest at the outset that his book does not fulfil these varied requirements. The natural difficulty of presenting the vast amount of detail contained in this subject in such a manner as not to embarrass the first-year student, and yet so as not to cause annoyance to the research worker through undue simplification of treatment, has not been entirely avoided.

The book contains sections on experimental technique, on volumetric, gravimetric and colorimetric analysis and on gas analysis: the amount of space devoted to electro-analytical and colorimetric methods is particularly welcome, and the author's description will engage the attention of those readers who are interested in the application of essentially physical methods of measurement to chemical problems. Each section contains a full account of a selected range of modern practical determinations, and cross-reference is made throughout to a careful and lengthy discussion of the theoretical bases underlying the several methods. It is unfortunate that it was impossible to include references to the original literature, as opposed to specialized monographs: an early acquaintance with this forms an invaluable part of the chemist's training, and the absence of references necessarily limits the interest which specialists are likely to take in the book.

The type and lay-out of the book are excellent, and it has been generously illustrated—indeed, certain of the diagrams appear superfluous (e.g. figures 5–1 and 5–2). Since such good use is made of cross-reference, it is suggested that page headings showing the section and paragraph numbers would have made this task much easier.

In conclusion, the book can be highly recommended to second- and third-year students: it should also prove useful to chemistry teachers in the higher forms of schools; certainly in few books that the reviewer has seen is the theory of this branch of chemistry so well interwoven with the study of the various practical methods.

R. F. B.

The Physics of the Divining Rod, by J. C. Maby and T. B. Franklin. Pp. xv+452. (London: G. Bell, 1939.) 21*s*.

Too many friends and acquaintances whose opinions I respect have had personal experience of dowsing for me to dismiss it summarily. Since this book promised to give a physical explanation of water divining with the evidence leading to it, I started to read it with particular interest, but have to confess that I was disappointed. The theory held by the authors is that water and metals, and indeed all electrical conductors, continuously emit Hertzian radiation, which they suggest is of wave-length about 10 metres, though

whether this is a universal figure, or whether the wave-length depends on the size of the deposit, and is usually of this order in water divining, I could not understand. The rays from these objects are believed by the authors to form patterns, after the manner of optical interference patterns, so that, for example, parallel to an underground stream there will be bands of reaction (*R*-bands) separated by neutral (*N*-) bands. In one place they attribute these to beats between two slightly different frequencies. In any case, the phase of the waves is liable to shift spasmodically, at intervals of seconds, minutes or hours, and the necessity for this assumption seems to me to undermine much of the evidence which the authors present. Thus on p. 146 there is a curve showing the fluctuations of earth potential in the neighbourhood of a stream, in which the damped sinusoidal form is very well marked. But suppose the results to be entirely random, though whenever at a point A the reading is high, the phase is considered normal, and when it is low at this point, the phase is said to have altered. Then a curve of these random readings will show an *R*-band at *A* and an *N*-band half a " wave-length " away. This is what appears to have been done in this case, for we are told " Many traversals made during a steady period (allowing for changes of polarity), and then averaged. Resultant curve slightly smoothed." Is it surprising that the curve supports the thesis put forward? On the other hand, that there is something objective seems to be proved by another line of argument developed by the authors. They find that the variations in " field strength " can be detected by several forms of electrical instrument, and when these are used, the fluctuations in the readings of one instrument appear to be correlated with those of others of different types. Whether the fluctuations, and indeed the readings themselves, are really to be associated with the presence of ores or water, or whether the instruments are really detecting cosmic rays or responding to some other influence, is perhaps a question which still needs further investigation, but the authors do appear to be on firmer ground in this part of their work.

It is really impossible in a short review to give a proper account of the whole book, and those who are interested may well be recommended to study it at first hand. It can, however, be said that the authors would obtain the ear of physicists more readily if they omitted some of the preliminary historical matter and refrained from implying belief in those psychic dowsers who can detect where water will be found by passing instruments over a *map* of the locality concerned. Possibly, indeed, a systematic presentation of the experimental results, and of their interpretations, might have been best achieved by publication as a series of papers to some recognized scientific society, where they could have been discussed openly. Nevertheless, the authors have chosen book form, and since this is probably the most scientific study of the subject yet published, it deserves consideration by all who are seriously interested in the matter. J. H. A.